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# RECYCLE OF PAPERMILL WASTE WATERS AND APPLICATION OF REVERSE OSMOSIS

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RECYCLE OF PAPERMILL WASTEWATERS AND APPLICATION OF REVERSE OSMOSIS

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Pilot plant reverse osmosis units were operated on weak waste waters from a pulp and paperboard mill to obtain further data on R.O. as an integral part of a closed water system within the mill. Of the many equipment types tested, the one selected was capable of concentrating a stream containing 1% dissolved solids to 99% less volume containing 10% dissolved solids. Product water thus separated was of high quality, suitable for use for stock dilution, pump shaft seal lubrication, etc. Overall flux rate for the operating portion of a plant performing to these standards was about 7 gallons/ft$^2$/day. The cellulose acetate membranes exhibited no significant deterioration, and a conclusion that the membranes are capable of providing a minimum of one year of continuous service is encouraged. Limited testing at higher temperatures indicated that the membranes do not deteriorate as rapidly as predicted. It is concluded that further development and commercialization will result in plants that approach the performance of industrial process equipment. (Lowry-Texas)

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# RECYCLE OF PAPERMILL WASTE WATERS AND APPLICATION OF REVERSE OSMOSIS

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## ABSTRACT

A program is in progress involving the closure of a pulp and paperboard mill and includes the recycle and re-use of weak waste waters. These waste waters, containing dissolved organics, occur as a consequence of normal production methods in such a mill. A method of recycling weak waste waters has been developed and incorporated that results in the reduction and partial concentration of the waste stream. Reverse osmosis is being investigated for use as a unit operation in which clarified water is separated from the remaining wastes for process re-use, and the organics are concentrated for processing by more conventional techniques.

To ensure that the production reverse osmosis facility would reflect the latest technology, the project required a pilot phase in which reverse osmosis vendors would operate proprietary equipment simultaneously and continuously on the same feed. This preliminary phase allowed the development of operating techniques applicable to this particular feed. Criteria were determined for the design of a full-scale production facility. The proprietary equipment designs of the participating vendors were assessed.



This report is submitted in partial fulfillment of Program No. 12040 FUB under the partial sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

KEY WORDS: Reverse osmosis, recycle, membrane process, organics removal.

CONTENTS


| Section | | Page |
|---|---|---|
| I | Conclusions | 1 |
| II | Recommendations | 3 |
| III | Introduction | 5 |
| IV | Recycle Development | 9 |
| V | Recycle Results | 13 |
| VI | Reverse Osmosis Equipment Description | 17 |
| VII | Test Specifications and Procedures | 25 |
| VIII | Process Investigation | 33 |
| IX | Discussion of Process Investigation | 69 |
| X | Special Processing--High Temperatures | 73 |
| XI | Equipment Evaluation | 75 |
| XII | Equipment Discussion--Mechanical Performance | 81 |
| XIII | Acknowledgments | 83 |
| XIV | Appendices | 85 |




Preceding page blank

FIGURES (continued)


| | | Page |
|---|---|---|
| 23 | Flux Rate vs. Concentration of Feed (Unit Y) | 59 |
| 24 | Feed Soluble Solids vs. Product Water Soluble Solids | 62 |
| 25 | Feed Soluble Solids vs. Product Water Sodium | 63 |
| 26 | Feed Soluble Solids vs. Product Water $BOD_5$ | 64 |
| 27 | Feed Soluble Solids vs. Product Water Color | 65 |
| 28 | Feed $BOD_5$ vs. Product Water $BOD_5$ | 67 |
| 29 | Conductivity vs. Product Water $BOD_5$ | 68 |

TABLES


| No. | | Page |
|---|---|---|
| 1 | Recycle Data | 14 |
| 2 | Tests Scheduled and Completed, Aqua-Chem Unit | 26 |
| 3 | Tests Scheduled and Completed, American Standard Unit | 28 |
| 4 | Tests Scheduled and Completed, Gulf Unit | 29 |
| 5 | Tests Scheduled and Completed, Havens Unit | 30 |
| 6 | Membrane Productivity Changes | 34 |
| 7 | Percent Rejections Experienced on All Units | 61 |

# SECTION I

## CONCLUSIONS

Recycle techniques have been incorporated that substantially reduce the volume of waste waters. Significant problems have resulted from this extensive recycle, and further refinements will be necessary.

The reverse osmosis process is effective in concentrating the dilute waste water stream while producing a clarified water flow that can be utilized for process purposes. The process is capable of concentrating a stream containing 1 percent dissolved solids to 90 percent less volume containing 10 percent dissolved solids. The product water thus separated is of high quality and can be utilized for stock dilution, pump shaft seal lubrication, etc. The overall flux rate for the operating portion of a plant performing to these standards is about 7 gallons/ft$^2$/day.

Operating techniques, such as maintaining a certain velocity, have been developed and can control the tendency to foul the membranes with materials in the feed stream. These techniques must be incorporated in any production process planned. Further, the resultant production plant would have to be constructed such that further refinement of the flux regeneration techniques could be undertaken. There are many portions of the process that are not well-defined, and a production operation would initially involve a program of continuing development.

The cellulose acetate membranes exhibited no significant deterioration, and a conclusion that the membranes are capable of providing a minimum of one year of continuous service is encouraged. The limited testing at higher temperatures indicated that the membranes do not deteriorate as rapidly as predicted.

The reverse osmosis process equipment will perform adequately with a tolerable maintenance cost, but opportunities for improvements to meet industrial standards are apparent. It is concluded that further development and commercialization will result in plants that approach the performance of industrial process equipment.

## SECTION II

## RECOMMENDATIONS

It is recommended that efforts continue to reduce and eliminate the problems resulting from the high degree of waste water recycle. Duplication of some items of equipment, monitoring and control devices, and greater surge capacity will be required to ensure constant ard adequate reduction of the waste water losses.

It is recommended that reverse osmosis be considered for incorporation in the mill process if other steps taken to reduce the waste stream are insufficient to bring the total mill effluent within the allowable standards set by the enforcement agencies.

Because the application of the reverse osmosis process has not been previously demonstrated, a reverse osmosis production plant must be compatible with main plant process variations and equipment modifications. Hence, the prime consideration in judging competitive designs must be system engineering, presuming that the cost differences among several vendors would be reasonably close. A production plant should be considered an integral part of the overall manufacturing facility, and its design must incorporate similar reliability goals.

It is recommended that very tight supervision of the entire design, construction, and start-up be maintained by Green Bay Packaging since the reverse osmosis equipment suppliers do not have broad experience in the field of industrial process plant engineering.

It is recommended that process development pilot operations continue until the production plant is considered totally operational. The process techniques developed during the brief pilot phase require refinement and verification. Also, the significant cost reductions offered by higher temperature operational capability are important, and pilot investigations of this aspect should continue.

Regardless of further action taken by Green Bay Packaging, it is recommended that encouragement be given for further development of the reverse osmosis process. The prospect of significant advancement in the field of pollution abatement warrants the extensive sustained development programs that will be required to apply the process to complex waste streams.



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## SECTION III

## INTRODUCTION

In June, 1970, Green Bay Packaging Inc. was awarded a Research, Development, and Demonstration Grant by the Office of Research and Monitoring of the Environmental Protection Agency. The grant is in support of a project to recycle weak waste waters in the Green Bay mill, utilizing a reverse osmosis plant as a tool in the normal production scheme.

The company operates a pulp and paperboard mill adjacent to the Fox River in Green Bay, Wisconsin. The mill utilizes the neutral sulfite semichemical process to produce fiber pulp from hardwoods. The pulp, suspended in water, is dispersed on a forming screen to produce paper and the bulk of the drained water is returned to process. These operations utilizing water as a carrier fluid result in the dispersion of dissolved organics in the water. The majority of the organics may be collected in a concentrated form and are treated conventionally by evaporation and combustion. A portion of the organics are in a very dilute solution; the excess and loss of these weak waste waters creates a stream pollution load.

The mill had been under state orders since 1957 to reduce the mill effluent discharge to no more than 22,684 pounds of biochemical oxygen demand ($BOD_5$). Soon after the FluoSolids combustion system was constructed, this requirement was met. Green Bay Packaging has had a long standing goal of maximum pollution abatement and consequently expected more stringent restrictions. Three routes were taken in searching for more complete abatement--electrodialysis, reverse osmosis, and activated sludge sewage treatment. Electrodialysis proved impractical for technical reasons and the investigation of it was terminated.

The company became one of four local mills involved with the local Metropolitan Sewerage District in research of joint industrial-municipal sewage treatment. At the same time, investigation of reverse osmosis was being done throug the agency of the Institute of Paper Chemistry. Both programs included demonstration as well as research and development and involved industry and government, with partial support from the Environmental Protection Agency.

These early efforts included the operation of two pilot reverse osmosis units at the mill. The goals of this



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process investigation were two-fold: first, to concentrate the weak wastes to the point that the existing conventional techniques could be used for disposal; and second, to extract a clarified stream suitable for process re-use or simplified disposal. This earlier work demonstrated that reverse osmosis was effective in separating wastes but that the equipment had not been sufficiently developed to be mechanically reliable, and that there were processing problems which resulted in a sizable loss of membrane productivity.

Since the trials indicated that the process might prove feasible, an investigation was begun to determine if the potential costs could be minimized by reducing the waste stream volume. The entire process water system was surveyed; it was determined that the only sizable reduction would result if waste water could be substituted for fresh water supplied to the paper machine showers. Since such showers require a stream relatively free of suspended matter, it was necessary to evaluate clarification equipment. Various shower nozzle designs were also tested. The investigation demonstrated that waste waters could be recycled, although it was not possible to evaluate the impact upon the papermaking process, maintenance costs, and product quality. Nonetheless, it was decided to recycle waste waters to the machine showers and several other minor uses.

Green Bay Packaging Inc. was successful in obtaining another reverse osmosis pilot unit in early 1970, and several concepts of maintaining membrane productivity were soon verified. Also, the unit demonstrated an improved mechanical integrity.

Investigation into joint industrial-municipal sewage treatment had proceeded at the same time as the reverse osmosis study. It was found that joint treatment was technically feasible for meeting the requirements of the enforcement agencies.

The immediate goals of pollution abatement to be attained were defined in the new State Orders received in December, 1969. These orders required that by the end of 1972, the mill discharge could not exceed 35.0 pounds of $BOD_5$ per ton of pulp produced, or 6934 pounds daily, whichever was least. The orders also set a limit of 20 pounds of suspended fiber per ton of paper produced, or 1.0 percent of machine production, again whichever was least.

The success of both the recycle trials and the most recent pilot plant led to a commitment to incorporate reverse osmosis in the mill process, and further effort on joint sewage treatment was terminated. Several reasons influenced the selection of the relatively unproven reverse osmosis process. Biological treatment does not destroy the color bodies (sulfonated lignin compounds) in the waste, and it has been assumed that color will be part of the defined criteria for judging effluent quality in the future. The combustion plant was available and had been expanded for possible disposal of wastes concentrated by reverse osmosis.

The company has had a long-standing policy of doing the best possible pollution abatement at the present and in the future. It was felt that a higher level of abatement could be accomplished by incorporating reverse osmosis. With a self-contained process independent of an outside agency, it would be possible to freely develop improvements. Also, water quality criteria may become more stringent and alternate processes might not be adequate.

The modular reverse osmosis concept is flexible and can be modified or varied as mill conditions change. Substantial improvements in equipment reliability, membrane performance, etc., are expected in the future. Finally, the estimated costs--capital, operating, etc.--for sewage treatment of this particular waste stream seem fairly close to those for reverse osmosis.

Having made the commitment to reverse osmosis, an application was made to the Environmental Protection Agency for the support of further development and the construction of a production unit. The grant was made June, 1970; and the project began employing a formal schedule of investigation.

To ensure that the production reverse osmosis facility would reflect the latest proven technology, the project required a pilot phase in which reverse osmosis vendors would operate proprietary equipment simultaneously on the same feed, on a continuous basis. This phase provided information for three requirements:

a. To develop operating techniques applicable to this particular feed.

b. To provide criteria for the design of a full-scale production facility.

c. To permit assessment of the proprietary designs of the participating vendors.

Contact had been made with several vendors prior to the grant; ultimately, four vendors elected to participate in the pilot phase of the program. They were:

a. American Standard, Hightstown, New Jersey. (Note - After entry into the program, the ConSeps Division of American Standard was purchased by Abcor, Inc., Cambridge, Massachusetts.)

b. Aqua-Chem, Inc., Waukesha, Wisconsin.

c. Gulf Environmental Systems, San Diego, California.

d. Havens International, San Diego, California. (Note - Havens was acquired by the Calgon Corporation, a subsidiary of Merck, and is now known as Calgon-Havens.)

The pilot phase was split into two segments. The first, from September 1 through November 30, 1970, was a trial period during which the vendors were free to gain experience and make modifications, improvements, substitutions, etc. The second segment ran from December 1, 1970, through February 28, 1971, and was designated the "frozen design" period because no improvements, modifications, or substitutions were permitted on the proprietary equipment. Maintenance was permitted, but records were kept for comparative evaluation. The vendors specified the test requirements--samples, pressures, etc.; data were collected and samples analyzed under the supervision of Green Bay Packaging. The data on each unit were made available to the specific vendor. The vendors were permitted to collect extra data and perform special tests with the approval of Green Bay Packaging.

The quantity of reverse osmosis data acquired by Green Bay Packaging personnel is too great for complete inclusion in this report. Summaries of data will be presented as well as specific examples to illustrate the observed performance. The process data cited should not be used for evaluation of a vendor except where noted. Most of the tests resulted in conclusions on principles that would apply to any reverse osmosis unit.

## SECTION IV

## RECYCLE DEVELOPMENT

Reverse osmosis trials performed in 1969 indicated that the process could be applied to the weak waste waters, although it would require further development. The process was also expensive, and a reduction in the volume of wastes offered obvious advantages. Thus, all the mill process streams were surveyed. Much of the waste water was already being recycled for repulping, stock dilution, and similar operations. It was determined that the only substantial volume reduction possible was the substitution of waste water for fresh water fed to the wire cleaning showers on the paper machine.

These showers are utilized for cleaning the wire on its return path; the high pressure stream removes any entrapped debris to ensure proper drainage of the pulp slurry in the sheet-forming section. The showers have very small openings; waste waters containing fibrous matter plug the nozzles quickly. Also, the fibrous matter that passes through the nozzle tends to accumulate on machine components.

Originally, a portion of the waste water had been partially clarified using a flotation technique. The gradual closure of the mill water loop over several years had resulted in increased water temperatures. The flotation process became less effective, and a new clarification step was devised in 1968. The waste stream containing large quantities of fine fiber was utilized as dilution water for repulping kraft (corrugated) clippings. The repulped stock was supplied to the vacuumless (seal leg type) pulp thickener. The thickened fibrous mat formed on the thickener drum proved effective in removing a high percentage of the fine suspended matter.

The filtered waste stream coming from the pulp thickener required further reduction of the fiber rubble and virtually complete removal of the remaining long fiber if it was to be used for showers. A program was initiated late in 1969 to find a method for additional fiber elimination and to determine if there were shower nozzles available that would resist plugging or were simple to clean.

By mid-1970, many types of conventional devices for the removal of suspended matter--screens, filters, strainers,

etc.--had been tested at the mill. It was determined that a slotted screen (DSM, marketed by Dorr-Oliver, Inc.) removed almost all remaining long fiber. Several shower nozzle designs were evaluated. The Bird Aqua-Purge nozzle was found to remain open for long periods and to be easily cleaned.

These two items were incorporated in a major redesign of the mill water system to permit recycling of waste water to the paper machine showers. Figure 1 shows the key waste water flows before the revisions, and Figure 2 indicates the system presently in use. The design effort and modifications included far more than the incorporation of new screens and nozzles. The entire water system was overhauled. Sewers were re-routed to prevent losses, new tanks were required for surges, and extensive controls were installed to ensure a constant supply to the showers as well as to reduce the possibility of accidental losses.

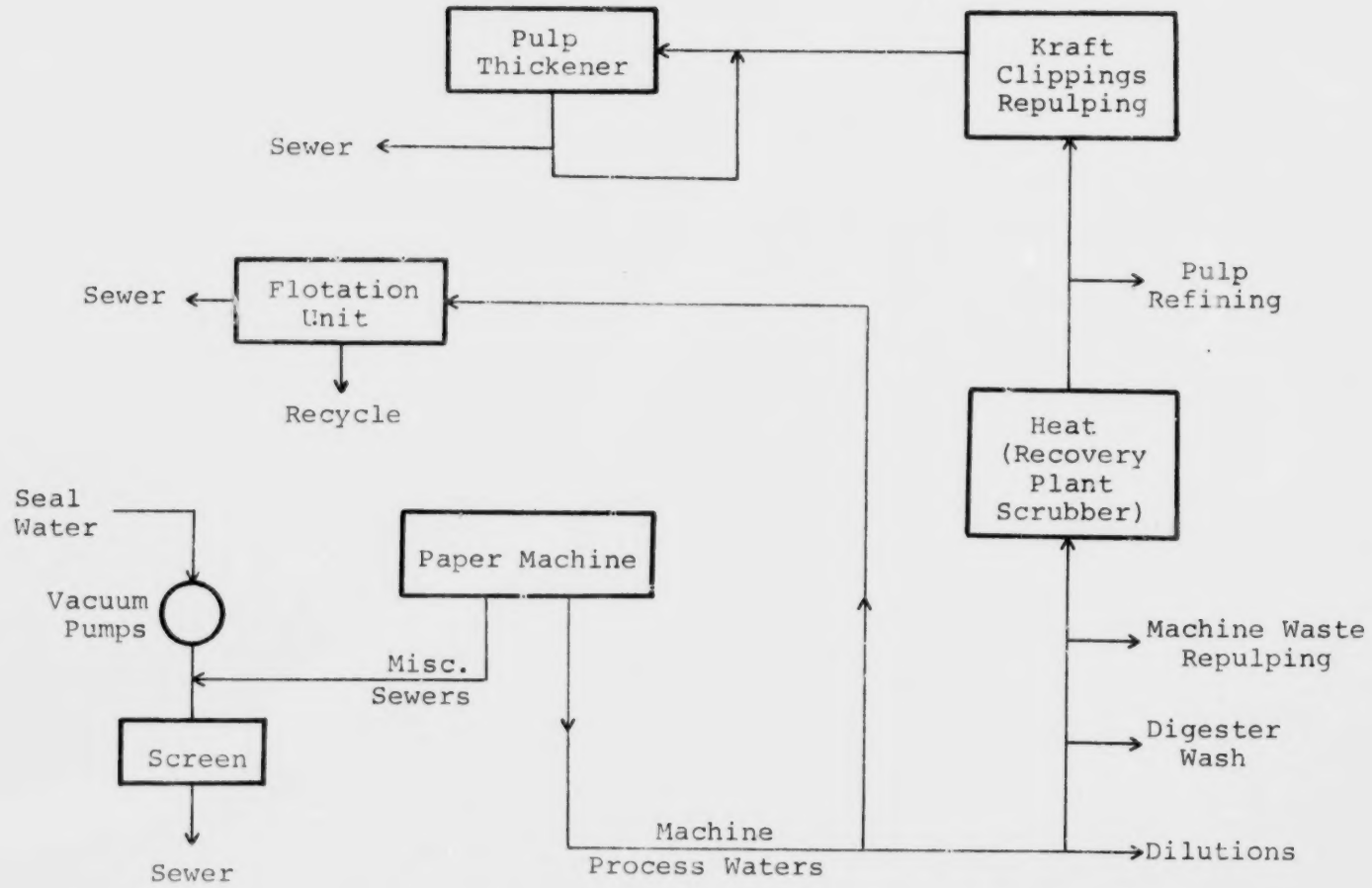


Figure 1. PROCESS WATER SYSTEM--1967

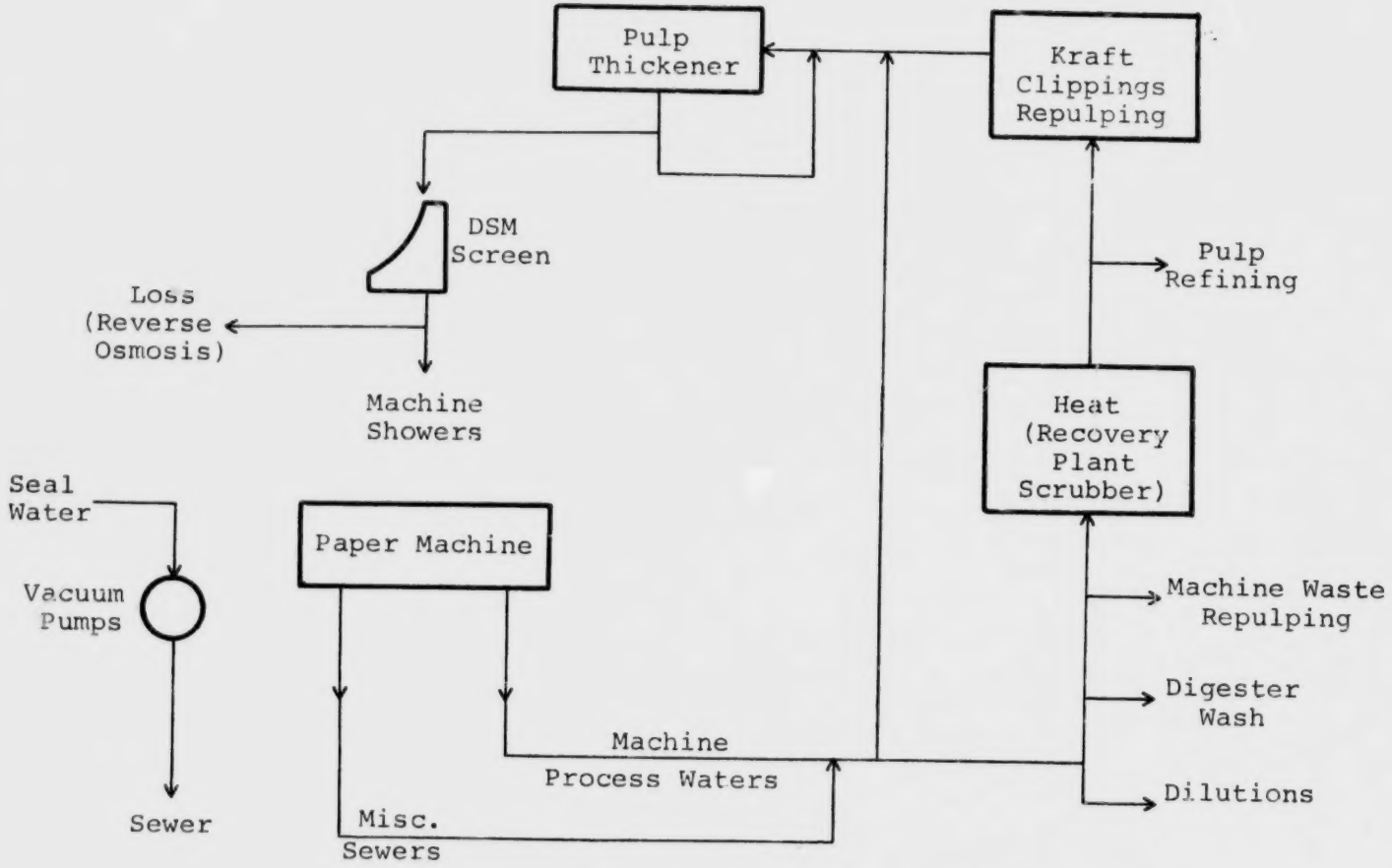


Figure 2. PROCESS WATER SYSTEM--1971

## SECTION V

## RECYCLE RESULTS

Waste water was first substituted for fresh water supplied to the machine showers in February, 1971, when the reverse osmosis "frozen design" period was almost complete. Several problems were encountered, including accumulations of fines in unagitated areas, cool spots promoting the growth of slime, mechanical breakdowns, and so forth. These were solved, and the shower water recycle program has been essentially continuous since April, 1971. In addition to the substitution at the showers, several other low-volume fresh water uses became evident and further recycling was accomplished. The characteristics of the waste water and the impact of recycle are indicated in Table 1.

After the initial difficulty with slime formation, routine addition of slimicide to the recirculating waters was begun. The quantity of slimicide has been substantially reduced. It is maintained primarily as insurance against the occurrence of unusual conditions that would promote slime growth. No change has been necessary in the defoamer agents added routinely at certain points in the process. An increase has been noted in the consumption of wet-strength resins required for certain grades of paperboard.

The quality of paperboard has remained satisfactory in the relatively brief time in which extensive recycle has been practiced. Long-term effects and the impact of seasonal variations in the fiber supply have not been determined.

Clouds of vapor and mist are characteristic around a paper machine wire section. These waters of varying solids content collect and fall at different points--above the machine, on catwalks, shower pipes, etc. After waste water re-use began on the showers, the combination of higher temperatures, more vapor, mist with a high solids content, and inadequate air flow resulted in many operating problems. The primary problems were breaks in the machine wires, shortened wire life (number of days in service), more frequent breaks of the paper web, and discomforting working conditions. Many corrective actions were taken--shower pipes relocated, exhaust air system modified, and so forth. Most of the problems have been alleviated, but the wire life has been only partially improved. Further work is planned for modifications around the machine and to evaluate other "wire" fabrics which will tolerate the new conditions.

Table 1

RECYCLE DATA

| | Before Recycle | After Recycle |
|---|---|---|
| Waste Water Loss, gpm | 650 | 25 |
| Additional Recycle, gpm | | 625 |
| Process Water Dissolved Solids Content | 0.9% | 3.5% |
| Fresh Water Consumption, gpm (Including Boilers) | 970 | 610 |
| Process Water Temperature | 130°F | 155°F |

The other problem area that has become apparent is the necessity for better control of the entire recirculating water system. The impact of a human error or a pump failure, for example, was often minimal with the old system. With a high re-use rate, the water system is so tightly closed that a failure or error can cause serious imbalances rapidly. Closer monitoring, control, and automation of the water system will be necessary. Greater surge capacity will also be required.

In addition to close control of the water volumes, it may be necessary to regulate the quality of the water. Stability of the machine water characteristics, such as dissolved solids content, may be mandatory. Thus, there are indications that reverse osmosis might fulfill a control function. It would permit the removal and clarification of some water for stabilization of the main process stream.

## SECTION VI

## REVERSE OSMOSIS EQUIPMENT DESCRIPTION

The general arrangement of the major pilot equipment is shown in Figure 3. In addition, two small pilot units were fed an uncooled waste water in a program which is described separately in this report. The four main pilot plants were all fed from a common line.

The American Standard unit, illustrated in Figure 4, was supplied with 84 modules (approximately 798 $ft^2$ of membrane surface). Each module contained 18 tubes in series, bonded into stainless heads. The tubes contained turbulence promoters. The modules were arranged in fourteen parallel rows containing six modules in series, all fed from a common manifold and returned to a common manifold. The feed was pumped with a three-section plunger pump with a variable-speed drive; a bladder accumulator on the downstream side reduced pulsations. Following the backpressure valve, the concentrate flowed to the sewer or to a concentrate tank. During recycle operations for tests at high feed solids, the majority of the concentrate overflowed into the feed tank, and the remainder was metered from the bottom of the tank with a variable-speed pump. The product water (permeate) was initially collected in a low header; later in the program, a second elevated header was used for some modules while demonstrating the effect of flooded shrouds. The unit was originally provided for continuous operation and was later modified for a depressurization cycle.

The Aqua-Chem unit, illustrated in Figure 5, had 24 modules (864 $ft^2$); each module consisted of 36 eight-foot tubes, all in series. The modules were arranged in four parallel rows of six modules in series; the four rows were connected to common inlet and outlet manifolds. The feed was pumped by a three-section plunger pump with a variable-speed drive; a sleeve-type accumulator was used on the downstream side. Following the backpressure valve, the concentrate was led to the sewer or to a recycle receiver fitted with an adjustable weir which served as a splitting device allowing recycle of some concentrate into the feed tank during runs at higher concentration. The product water was initially collected from the main heads only; this was later modified for discharge from both ends of the modules in two rows (12 modules). The unit had a timing device that provided a depressurization period followed by flushing.



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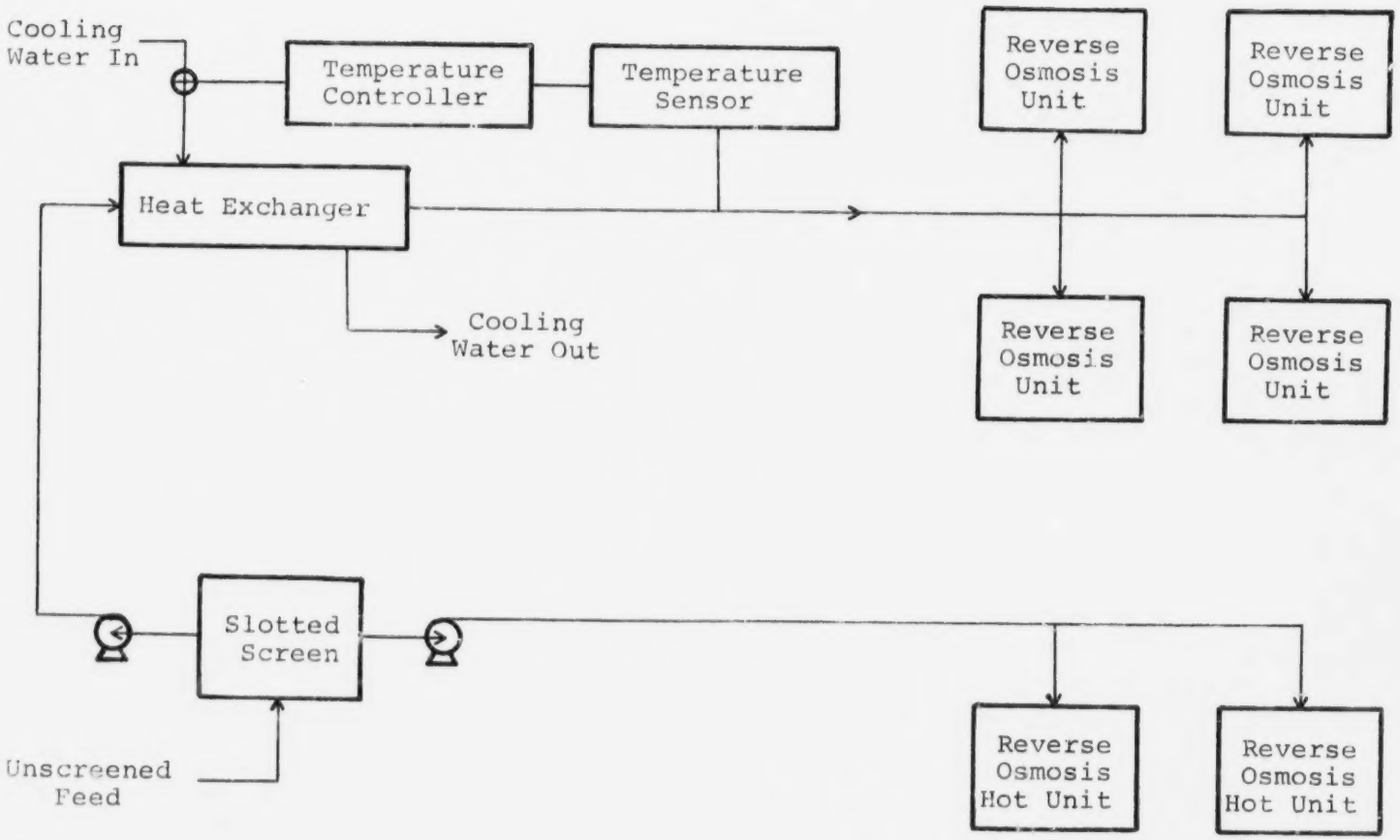


Figure 3. OVERALL EQUIPMENT ARRANGEMENT

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Figure 4. AMERICAN STANDARD UNIT

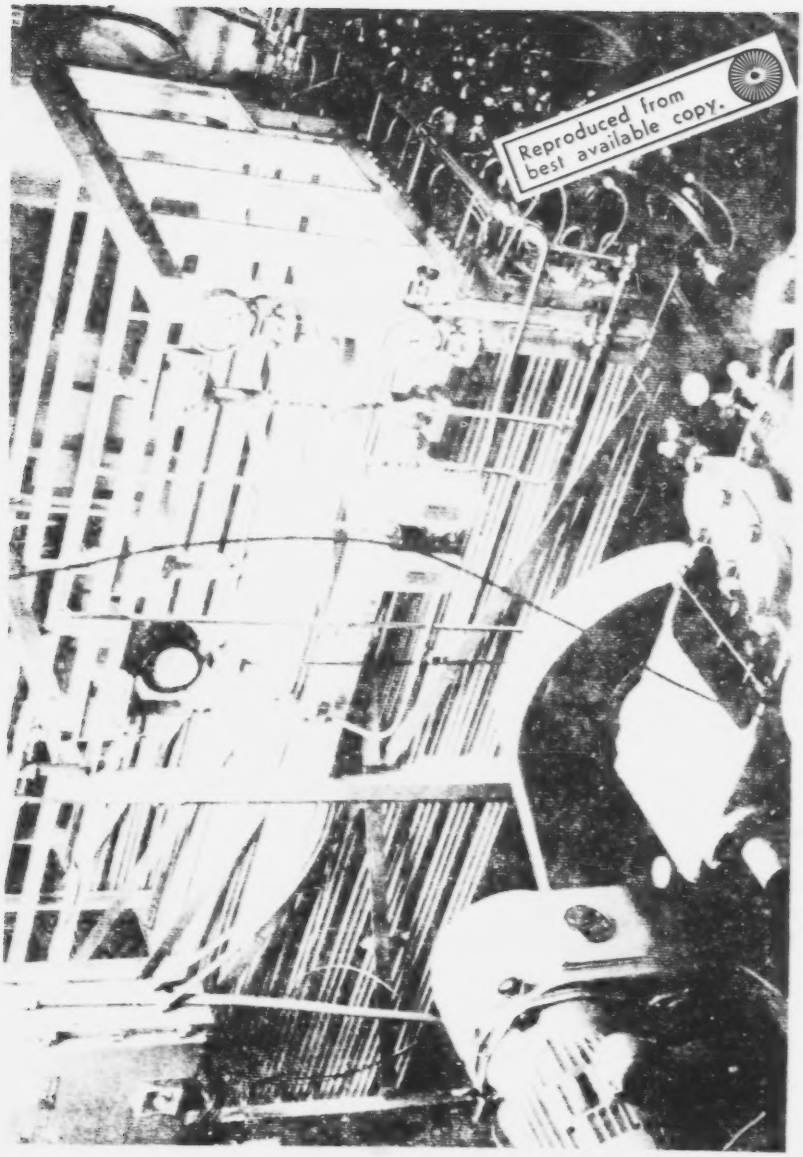
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Figure 5. AQUA-CHEM UNIT

Gulf provided two main units. The first was operated during September through November, 1970, and consisted of three spiral-wound modules in series (about 150 $ft^2$). The unit was fed by a plunger pump. Considerable experimentation was done with this unit, resulting in a major alteration of the proprietary module design.

The second Gulf unit provided for the "frozen design" trial, illustrated in Figure 6, consisted of 18 modules, 3" diameter, and three feet long. It contained about 900 $ft^2$ of membrane surface. Late in the period, three of the original modules were replaced with modules of smaller diameter in a smaller pressure tube. The feed pump was a multistage centrifugal with a fixed speed; volume adjustment and pressure control were obtained with valves. Following the backpressure regulator, the concentrate was split into two streams (recycle and sewered concentrate) utilizing ball valves. The system had a timing mechanism to control a pause cycle and a backflush cycle; a small pump was utilized for the latter. Product water was collected from groups of three modules.

The Havens unit contained 24 modules (432 $ft^2$) in six parallel rows with four modules in series, and it is shown in Figure 7. The modules contained 18 eight-foot tubes in series. The six rows were connected to common inlet and outlet manifolds. The feed was pumped with a three-section plunger pump with a variable-speed drive; a bladder accumulator was utilized on the discharge. Following the backpressure valve, the concentrate was led to either the sewer or a weir pot for splitting off a portion for recycle during runs at higher concentration. The product water from each row of four modules was passed to a common collector. The unit had a timing device for the depressurization cycle.

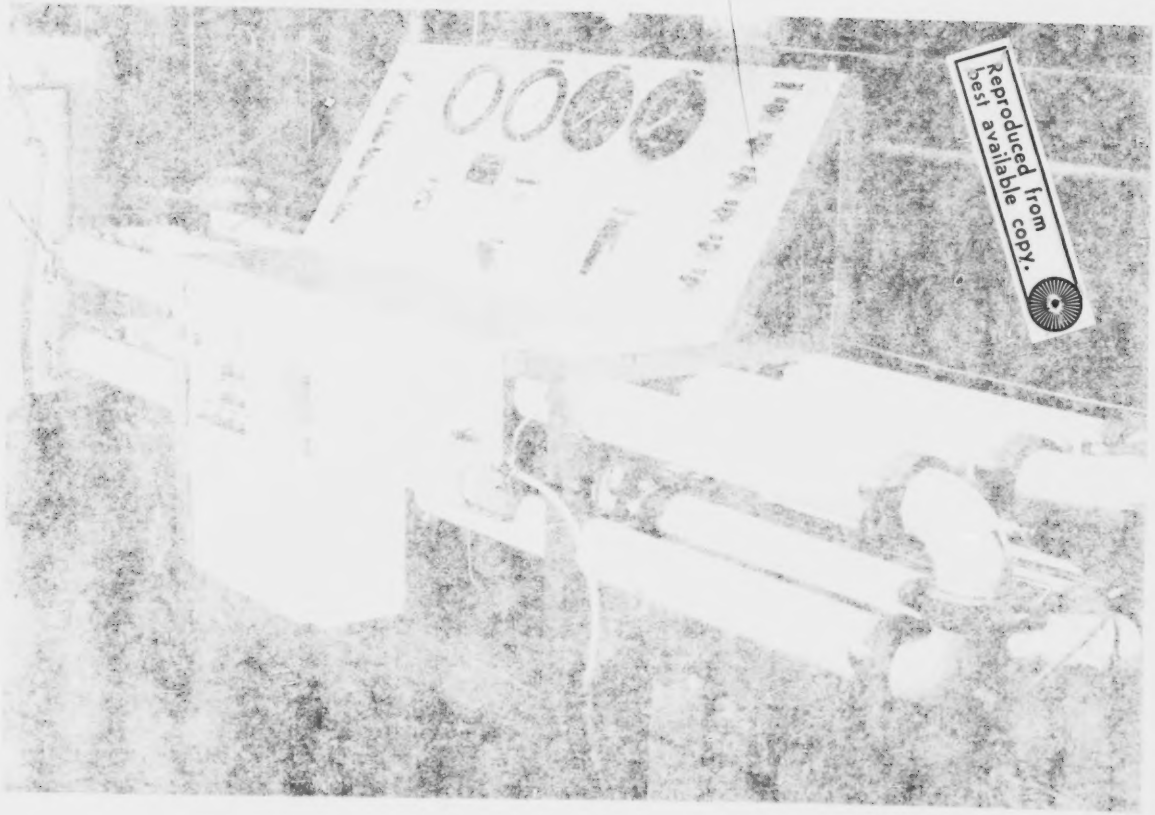
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Figure 6. GULF UNIT

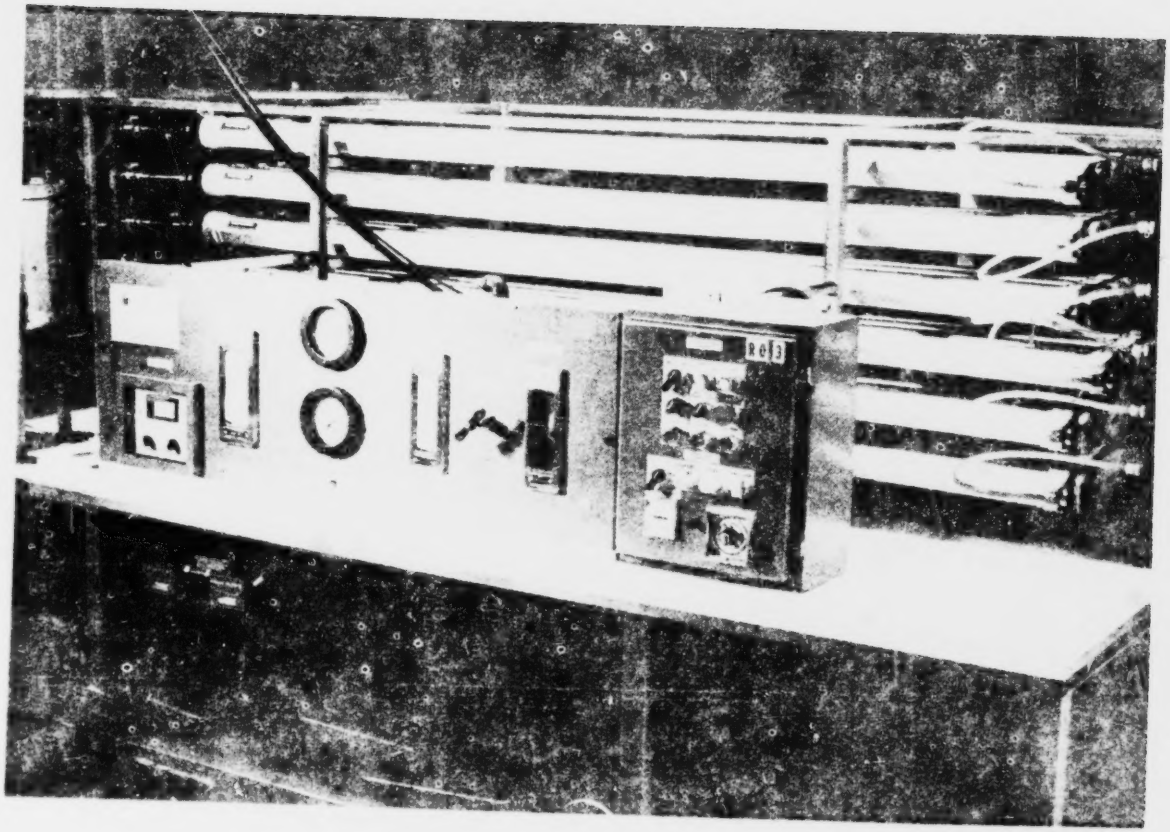

Figure 7. HAVENS UNIT

## SECTION VII

## TEST SPECIFICATIONS AND PROCEDURES

Each vendor originally submitted a specific test plan of the test conditions for the unit, analytical samples required, etc., to be followed during the second segment of the pilot phase. These scheduled tests are summarized in Tables 2 through 5, together with the tests actually accomplished.

The measurement of operating characteristics for each unit was done with the standard devices of process development--stopwatches, thermometers, etc. Measurements were taken frequently, averaging about five times daily per unit and included readings at various intervals between pause (depressurization) cycles. When analytical samples were not required, grab samples were frequently taken of feed and concentrate to ensure good correlation with observed data (see Figure 8, for example). Measurements were made every day including weekends. To ensure maximum running time, a qualified technical representative was on call during the night hours to respond to any problem or unusual condition reported by the mill operating supervision, who made periodic observations.

The analytical samples were composite or grab, depending upon the requirements of the vendors. Each was taken to coincide with the measurement of the unit characteristics. The analytical techniques are summarized in Appendix 1.


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Table 2

TESTS SCHEDULED AND COMPLETED

Aqua-Chem Unit

| Specified Conditions | | | Actual Test | | |
|---|---|---|---|---|---|
| Feed % Total Solids | Inlet Pressure psi | Feed Rate gpm | Feed % Total Solids | Inlet Pressure psi | Feed Rate gpm |
| City Water | 500 | 4 | City Water | 500 | 4.0 |
| City Water | 500 | 8 | City Water | 500 | 8.0 |
| City Water | 500 | 12 | City Water | 500 | 12.0 |
| 1.0 | 500 | 12 | 0.65 | 500 | 11.8 |
| 1.0 | 650 | 12 | 1.22 | 650 | 12.2 |
| 2.5 | 500 | 14 | 2.27 | 505 | 11.6 |
| 2.5 | 650 | 14 | 2.34 | 650 | 11.9 |
| 5.0 | 500 | 14 | 4.11 | 500 | 11.7 |
| 5.0 | 650 | 14 | 3.59 | 650 | 14.0* |
| | | | 4.85 | 650 | 12.0** |
| 7.0 | 500 | 13 | 6.12 | 550 | 12.1 |
| 7.0 | 650 | 13 | 5.61 | 650 | 12.9 |
| 9.0 | 500 | 13 | Unit Unable to Meet 9% at 500 psi, 13 gpm. | | |
| 9.0 | 650 | 13 | 6.71 | 650 | 13.0 |
| 1.0 | 500 | 10 | 0.85 | 500 | 10.1 |
| 1.0 | 650 | 10 | 1.02 | 650 | 10.6** |
| 2.5 | 500 | 10 | 1.71 | 500 | 9.7 |
| 2.5 | 650 | 10 | 2.96 | 650 | 9.8 |
| 5.0 | 500 | 10 | 4.61 | 505 | 10.4 |
| 5.0 | 650 | 10 | 3.79 | 650 | 10.2 |

Table 2 (continued)

TESTS SCHEDULED AND COMPLETED

Aqua-Chem Unit

| Specified Conditions | | | Actual Test | | |
|---|---|---|---|---|---|
| Feed % Total Solids | Inlet Pressure psi | Feed Rate gpm | Feed % Total Solids | Inlet Pressure psi | Feed Rate gpm |
| 7.0 | 500 | 10 | 5.40 | 500 | 10.5 |
| 7.0 | 650 | 10 | 4.90 | 655 | 10.4 |
| 9.0 | 500 | 10 | 8.10 | 500 | 10.2** |
| 9.0 | 650 | 10 | 8.14 | 650 | 9.9 |
| 1.0 | 500 | 7 | 0.81 | 500 | 7.2 |
| 1.0 | 650 | 7 | 0.66 | 650 | 6.8 |
| 2.5 | 500 | 7 | 2.30 | 500 | 7.2 |
| 2.5 | 650 | 7 | 2.92 | 650 | 7.0* |
| | | | 2.56 | 650 | 7.3 |
| 5.0 | 500 | 7 | 4.86 | 500 | 7.0 |
| 5.0 | 650 | 7 | 3.72 | 650 | 7.0 |
| 7.0 | 500 | 7 | 6.84 | 500 | 7.3 |
| 7.0 | 650 | 7 | 4.23 | 645 | 7.0* |
| | | | 6.78 | 650 | 8.0 |
| 9.0 | 500 | 7 | 7.76 | 500 | 7.0 |
| 9.0 | 650 | 7 | 6.40 | 650 | 6.7* |
| | | | 8.32 | 650 | 8.1 |
| 9.0 | 600 | Vary | Velocity and Pause Test | | |
| 1.0 | 650 | Vary | Velocity and Pause Test | | |

*Results Questionable--Test Repeated
**City Water Flux Measured After This Test

Table 3

TESTS SCHEDULED AND COMPLETED

American Standard Unit

| Specified Test | | | | Actual Test | | | |
|---|---|---|---|---|---|---|---|
| Total Solids Content | Pressure psi | Flow gpm | Duration | Total Solids Content | Pressure psi | Flow gpm | Duration |
| 1.0% Feed | 600 Exit | 4.2 Exit | 3 Weeks | 0.73% Feed | 600 | 4.2 | 5 Weeks |
| 5.0% Concentrate | 600 Exit | 4.2 Exit | 3 Weeks | 5.43% Concentrate | 600 | 4.1 | 5 Days |
| 9.0% Concentrate | 500 Exit | 4.2 Exit | 3 Weeks | Not Performed | | | |
| | | | | Unscheduled | | | |
| | | | | 9.00% Concentrate | 920 Inlet | 7.6 Inlet | 4 Days |
| | | | | 4.42% Concentrate | 920 Inlet | 7.6 Inlet | 1 Day |

Table 4

TESTS SCHEDULED AND COMPLETED

Gulf Unit

| Specified Test | | Actual Test | | |
|---|---|---|---|---|
| % Recovery | Duration | % Recovery* | Pressure psi | Duration |
| 50 | 7 Days | 84 | 400 | 8 Days |
| 75 | 7 Days | 77 | 460 | 23 Days |
| 83 | 7 Days | Not Performed | | |
| 90 | 7 Days | 87 | 600 | 7 Days |
| | | Unscheduled | | |
| | | 96 | 600, 800 | 5 Days |

*% Recovery Equals $\frac{\text{Permeate Volume}}{\text{Raw Feed Volume}}$ (100)

Table 5

TESTS SCHEDULED AND COMPLETED*

Havens Unit

| Specified Conditions | | Actual Conditions | |
|---|---|---|---|
| Feed % Total Solids | Velocity fpm | Feed % Total Solids | Velocity fpm |
| 1.0 | 4.0 | 0.7 | 3.9 |
| 1.0 | 4.5 | 0.7 | 4.5 |
| 1.0 | 5.0 | 0.8 | 5.0 |
| 1.6 | 4.0 | 1.2 | 4.1 |
| 1.6 | 4.5 | 1.0 | 4.5 |
| 1.6 | 5.0 | 1.4 | 5.0 |
| 3.0 | 4.0 | 2.8 | 4.0 |
| 3.0 | 4.5 | 2.2 | 4.4 |
| 3.0 | 5.0 | 3.4 | 4.9 |
| 4.1 | 4.0 | 3.8 | 4.0 |
| 4.1 | 4.5 | 3.3 | 4.5 |
| 4.1 | 5.0 | 3.6 | 4.8 |
| 6.5 | 4.0 | 5.3 | 4.0 |
| 6.5 | 4.5 | 4.4 | 4.3 |
| 6.5 | 5.0 | 4.9 | 4.9 |
| 9.0 | 4.0 | 7.9 | 4.0 |
| 9.0 | 4.5 | 8.6 | 4.5 |
| 9.0 | 5.0 | 7.7 | 5.0 |

*All Tests 48-72 Hours Duration, at 800 psi.

XXX Unit
Pause Cycle 14 Min./2 Hr.

| Date | 12/17 | 12/17 | 12/18 | 12/18 | 12/18 |
|---|---|---|---|---|---|
| Time | 1:00 p.m. | 1:25 p.m. | 9:40 a.m. | 10:30 a.m. | 1:12 p.m. |
| Clock Hours | 2981.1 | 2981.7 | 3001.8 | 3002.6 | 3005.3 |
| Run Hours | 370.4 | 371.0 | 391.1 | 391.9 | 394.6 |
| Reference to Pause | 10 Min. After | Mid Cycle | 20 Min. Before | 10 Min. After | Mid Cycle |
| Pressure ├ In | 550 | 550 | 650 | 650 | 650 |
| Pressure ├ Out | 300 | 300 | 330 | 335 | 365 |
| Temperature °C ├ Feed | 33.8 | 34.0 | 35.2 | 34.6 | 35.8 |
| Temperature °C ├ Conc. | 34.0 | 34.6 | 36.2 | 35.6 | 36.4 |
| Temperature °C ├ Avg. | 33.9 | 34.3 | 35.7 | 35.1 | 36.1 |
| Concentrate to Sewer ├ Ml/Sec. | 718/59.6 | 800/60.1 | 646/59.2 | 767/59.9 | 536/58.6 |
| Concentrate to Sewer ├ Flow--gpm | 0.191 | 0.211 | 0.173 | 0.203 | 0.145 |
| Total Concentrate ├ (2 Gal.) - Sec. | 11.5 | 11.8 | 10.5 | 10.2 | 11.6 |
| Total Concentrate ├ Flow--gpm | 10.417 | 10.152 | 11.429 | 11.765 | 10.363 |
| Recycled Concentrate--gpm | 10.226 | 9.941 | 11.256 | 11.562 | 10.218 |
| Product Water ├ (2 Gal.) - Sec. | 64.0 | 62.9 | 54.9 | 53.3 | 47.9 |
| Product Water ├ Flow--gpm | 1.875 | 1.908 | 2.186 | 2.251 | 2.510 |
| Product Water ├ Flux As Is | 3.125 | 3.182 | 3.645 | 3.753 | 4.187 |
| Product Water ├ Flux @ 35°C | 3.204 | 3.233 | 3.586 | 3.744 | 4.081 |
| Calculated Feed--gpm | 12.292 | 12.060 | 13.615 | 14.016 | 12.873 |
| Inlet Velocity--Feet/Sec. | 5.122 | 5.025 | 5.673 | 5.840 | 5.364 |
| Conductivity (Dis. Solids--ppm) ├ Hand Meter | 109 | 99 | 111 | 108 | 89 |
| Conductivity (Dis. Solids--ppm) ├ Unit Meter | 176 | 160 | 156 | 158 | 130 |
| Oven Solids Sample - % ├ Feed | - | 6.12 | - | - | - |
| Oven Solids Sample - % ├ Conc. | - | 7.02 | - | - | - |
| Analytical Sample | - | - | - | - | XXX-6 |

Figure 8. TYPICAL REVERSE OSMOSIS DATA SHEET

## SECTION VIII

## PROCESS INVESTIGATION

### Feed Characteristics

The feed stream may be described as a solution of wood extractives and sodium lignosulfonates characteristic of the NSSC hardwood pulping process. During the froze' design phase, the stream as received at each reverse osmosis unit contained 0.6 - 1.9 percent total dissolved solids and an average of 280 ppm suspended solids. The suspended solids are colloidal and suspended fiber debris as well as very short hardwood fibers.

The temperature of the feed supply line common to all units was normally 35-38°C. When a portion of the concentrate from a unit was recycled to increase the feed solids, the several characteristics of the total feed stream changed proportionately with one exception; since the concentrate is depleted of those low molecular weight organic compounds (primarily acetic acid) which pass the membrane, the average molecular weight of the total feed is increased.

### Initial Membrane Flux Loss

During early experience, it had been noted that the membranes would lose some productivity rapidly when first exposed to the waste stream. At one time it had been speculated that this was a result of fouling or concentration polarization; however, the loss still occurred after development of processing techniques which precluded these causes. Membrane productivity was measured before exposure to waste water and after several time intervals to determine if there was a permanent loss unrelated to processing problems. These tests were performed on both city water and waste water, with a preference for the former since the composition changes little. The tests were all performed at 600 psi inlet pressure and at constant velocity. Those tests performed with waste water were all about 0.9 percent dissolved solids. Conductivity of the product water was checked with a dissolved solids hand meter. Continued exposure to waste water resulted in a reduction in conductivity, indicating a tightening of the membrane and greater rejection of dissolved solids. The results on three sets of membranes are shown in Table 6.



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Table 6

MEMBRANE PRODUCTIVITY CHANGES

| Membrane Vendor | Set | Test Fluid | Hours Exposure To Waste | Other Conditions | Flux gfd @ 35°C | % Flux Change From Last Test | % Flux Change From Original |
|---|---|---|---|---|---|---|---|
| A | 1 | City Water | 0 | | 17.92 | | |
| | | | 15.3 | | 15.58 | | -13 |
| | | | 63.6 | | 12.85 | -18 | -28 |
| | | | 280.0 | | 11.59 | -10 | -35 |
| A | 1 | Waste Water | 0.2 | | 11.90 | | |
| | | | 15.3 | | 10.68 | | -10 |
| | | | 58.0 | | 9.90 | -7 | -17 |
| | | | 59.0 | Immediately After 5 Days Rest | 10.33 | +4 | -13 |
| A | 2 | City Water | 0 | | 10.03 | | |
| | | | 285.0 | | 5.78 | | -42 |
| | | | 443.0 | | 6.25 | +8 | -38 |
| | | | 600.0 | Immediately After 4 Days Rest | 7.05 | +13 | -30 |
| | | | 911.0 | | 6.30 | -11 | -37 |
| | | | 1288.0 | | 6.84 | +9 | -32 |
| | | | 1724.0 | After Deliberate Fouling | 4.76 | -30 | |
| A | 2 | Waste Water | 0.4 | | 11.93 | | |
| | | | 42.0 | | 10.68 | | -10 |
| B | 1 | City Water | 0 | | 12.99 | | |
| | | | 270.0 | After 24 Hour Rest | 9.59 | | -26 |
| B | 1 | Waste Water | 0.5 | | 10.82 | | |
| | | | 49.0 | | 8.54 | | -21 |
| | | | 183.0 | | 8.56 | | No Change |
| | | | 270.0 | After 24 Hour Rest | 9.47 | +11 | -12 |
| | | | 560.0 | | 8.67 | -8 | -20 |

Even these measurements are not ideal since some were made after extensive process manipulation. However, it is evident that the membranes undergo a considerable tightening resulting in the reduction of the flux rate as a consequence of exposure to the waste water. Since part of the lost productivity is recovered after a rest period, it appears that there is a loss caused by compaction in addition to a permanent loss. For example, the membranes from Vendor B indicated a permanent loss of nine or ten percent when exposed to waste water and a further loss of about 10 percent when exposed to pressure with this latter loss recovered after resting.

The data also reflect an inconsistency in that the measurements made with both feeds--city water and waste water--do not always reflect the same amount of loss for the same amount of exposure.

Membrane Fouling

During the 1968-1969 investigative work at Green Bay Packaging, physical fouling of membranes had been observed; this fouling consists of colloidal and suspended fiber material which deposits on the membrane surface. This early experience indicated but did not prove that the minimum velocity was higher than expected; that some fouling was inevitable at any practical operating condition; that pausing (depressurizing) caused a restoration of the loss of productivity; and that permitting fouling to continue beyond some limit would result in a substantial permanent loss of productivity.

A primary purpose of the pilot phase was to better define the processing techniques which would permit control, if not elimination, of the fouling. Complete removal of the fiber rubble to preclude fouling is well recognized as a very costly operation and could not be considered if costs were to be minimized.

Prior to the pilot phase, all vendors were informed of our general experience with fouling and the partially-proven techniques which apparently could control it. It should be noted that this form of fouling is not necessarily unique to our feed, but the techniques evolved for prevention and control may be unique to the characteristics of our waste. The following control techniques and requirements were defined as a result of the pilot phase:

a. Pause Requirement

There is a distinction between a rest period and a

pause. The rest period lasts several hours, during which membrane compaction may lessen. The pause (depressurization) cycle is brief but sufficient for osmotic flow to take place.

The absolute necessity for a pause was illustrated on two units. The first unit was initially operated with an adequate velocity but a very short pause (depressurization) cycle--2.5 minutes down after 90 minutes running. After forty-five hours operation, the flux rate had dropped 49 percent. The pause duration was then changed to 8.25 minutes for the same run time; within four hours, the flux rate recovered 55 percent for a net loss of 20 percent from the original (new) productivity.

The second unit utilized turbulence promoters which, it was claimed, eliminated any tendency to foul. This pilot plant had no timing control or depressurization mechanism. Upon being exposed to sustained running, the unit lost flux rapidly. Manually pausing (shutting down) one to four times daily helped reduce the overall rate of decay; but after 563 hours, the unit lost 65 percent of the original productivity and after 760 hours, 78 percent.

b. Complete Depressurization

The pause cycle that has evolved during these studies has required full depressurization of the unit. It was demonstrated that a positive bleed was required. If the system remained closed between a backpressure valve and a plunger pump, for example, the unit pressure would rise to the osmotic pressure and then the "lifting" of fouling would cease. It was necessary to eliminate flushing cycles or to ensure that there was a period of depressurization before flushing since even low pressures reduced the effective osmotic flow. [It is worth noting also that flushing after a pause had no effect on membrane restoration or in inhibiting the resumption of fouling upon repressurization.]

Booster pumps utilized on the suction side of positive displacement pumps also had to be interrupted during the pause.

c. Pause Frequency

The pausing frequency was found to be once every 60 to 120 minutes, depending upon the preference

of the vendor, the velocity past the membrane surface, the amount of pause time, etc. A typical plot of water productivity through an entire time cycle on a unit being properly paused is shown in Figure 9. As time progresses after depressurization (pause), the flux rate drops for about ten minutes and then levels off and remains relatively constant for thirty to ninety minutes (the duration depending upon conditions and configuration). The flux rate then begins to drop, and the unit again requires depressurization.

The velocity and turbulence at the membrane surface obviously influence the accumulation of fouling. The average velocity through all tubes employed on one tubular unit exceeded 5.1 feet per second. Nonetheless, sufficient fouling occurred to produce a 7 percent loss in flux rate over a ninety-minute period. On a second tubular unit operating at 4.8 feet per second average velocity, fouling caused a 4 percent loss over a seventy-minute period. None of the four pilot plants was operated at higher velocities because of equipment limitations and also because the pressure drops can become excessive.

Upon repressurization after a pause, the loosened fouling does not immediately and completely migrate to the membrane surface. If such were the case, the flux would rapidly drop to the value that existed before pausing. As illustrated in Figure 9, the flux degradation occurs over several minutes until the normal productivity level is reached.

Flushing after pausing might be expected to sweep away fouling that was loosened by osmotic action during the pause. As part of the investigation of the operating cycle, a unit was operated with and without flushing between the end of pause and beginning of repressurization. The characteristic curve shown in Figure 9 was unchanged by the inclusion of a flushing step.

It was observed that membranes which became somewhat permanently fouled required the shorter total running cycles (60 minutes vs. two hours).

d. Pause Duration

The duration of the pause cycle is dependent upon the other processing variables, such as velocity. Nonetheless, the vast quantity of data taken under

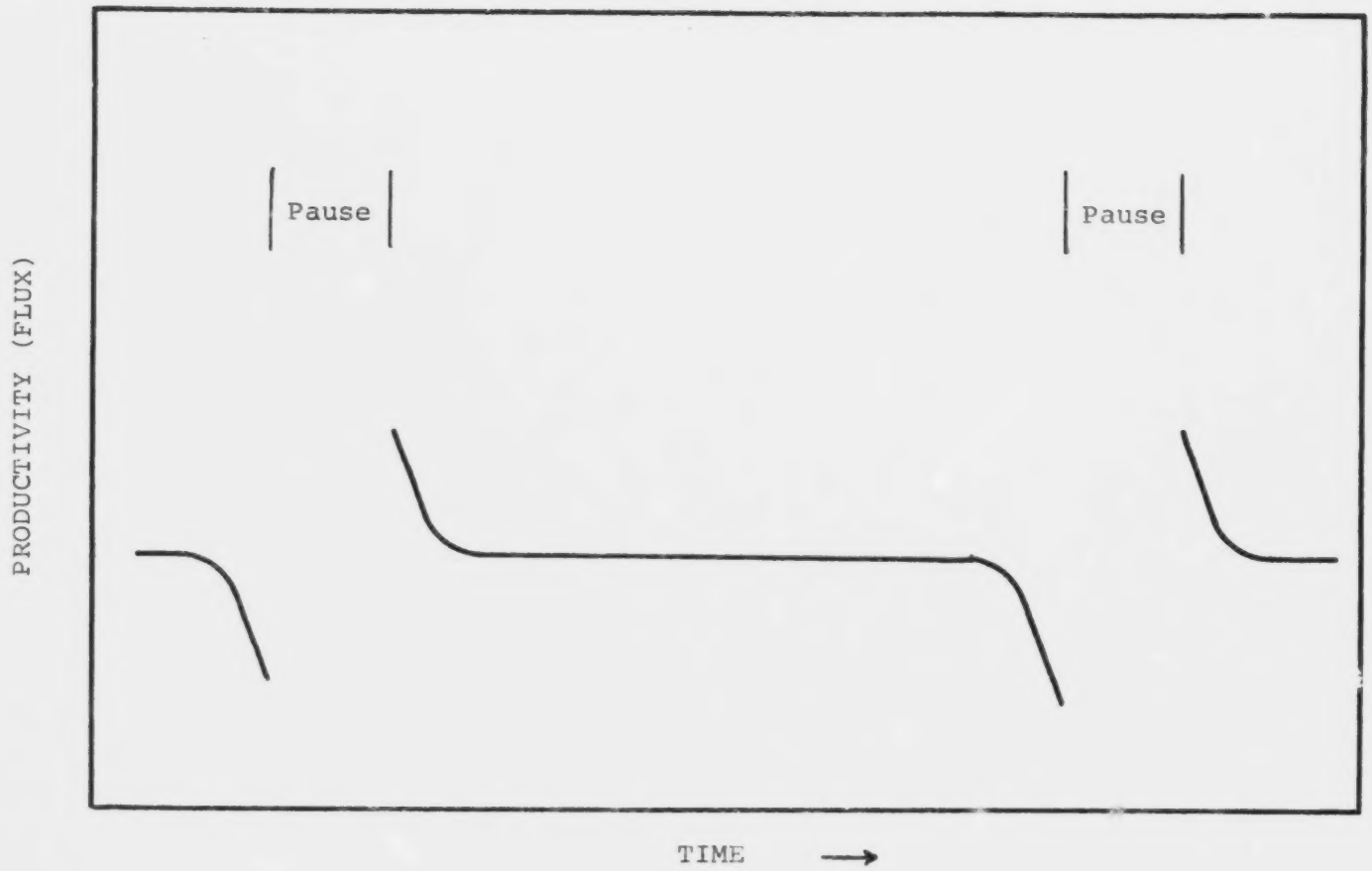


Figure 9. SHORT-TERM MEMBRANE PRODUCTIVITY VS. TIME

numerous conditions on four units has indicated similar minimum pause time requirements.

Several attempts were made to define the minimum pause time as well as the minimum velocity. As noted in the subsection "Pause Requirement", one unit was started with a very inadequate 2 1/2 minute pause time. The flux began to recover when the time was adjusted to 8.25 minutes. The optimum time eventually proved to be twelve minutes on this unit.

Two sustained runs were made on one unit. The first was performed with a feed of about 9 percent solids over fifteen days (see Figure 10). After several days of erratic performance, a base line was established using a fourteen-minute pause (two-hour total cycle). The pause time was then reduced to twelve minutes and the flux began to decline. The velocity was then increased to 4 feet per second and the flux rate improved.

The second test (Figure 11) was performed with a feed of about 1.5 percent solids. After two days of irregular performance, the unit stabilized. The flux rate was normal compared to previous runs at the same conditions. The velocity was relatively low at 3 feet per second, and the pause was set at 14 minutes (two-hour total cycle). The pause was changed to twelve minutes, and some loss of productivity was noted. A further reduction to ten minutes was made with flux deterioration becoming quite evident after about three days. The velocity was then increased, and the flux rate improved noticeably. Soon after, the high pressure pump began to perform erratically. The feed rate (and thus the velocity) would drop off sharply and later return to normal. During the night hours, this would go undetected when it did not coincide with the periodic observations by the mill supervisory personnel. Permanent or stable fouling evidently occurred at this time, and a final adjustment of the pause to fourteen minutes was ineffective.

We have observed in these runs that the effect of revising an operating limit is often not evident for two or three days. The tests are difficult to perform since many variables--pump speed, feed solids, etc.--are constantly changing; and even when several points of data are taken under apparently identical conditions in a short time, there will be a wide variation in results.

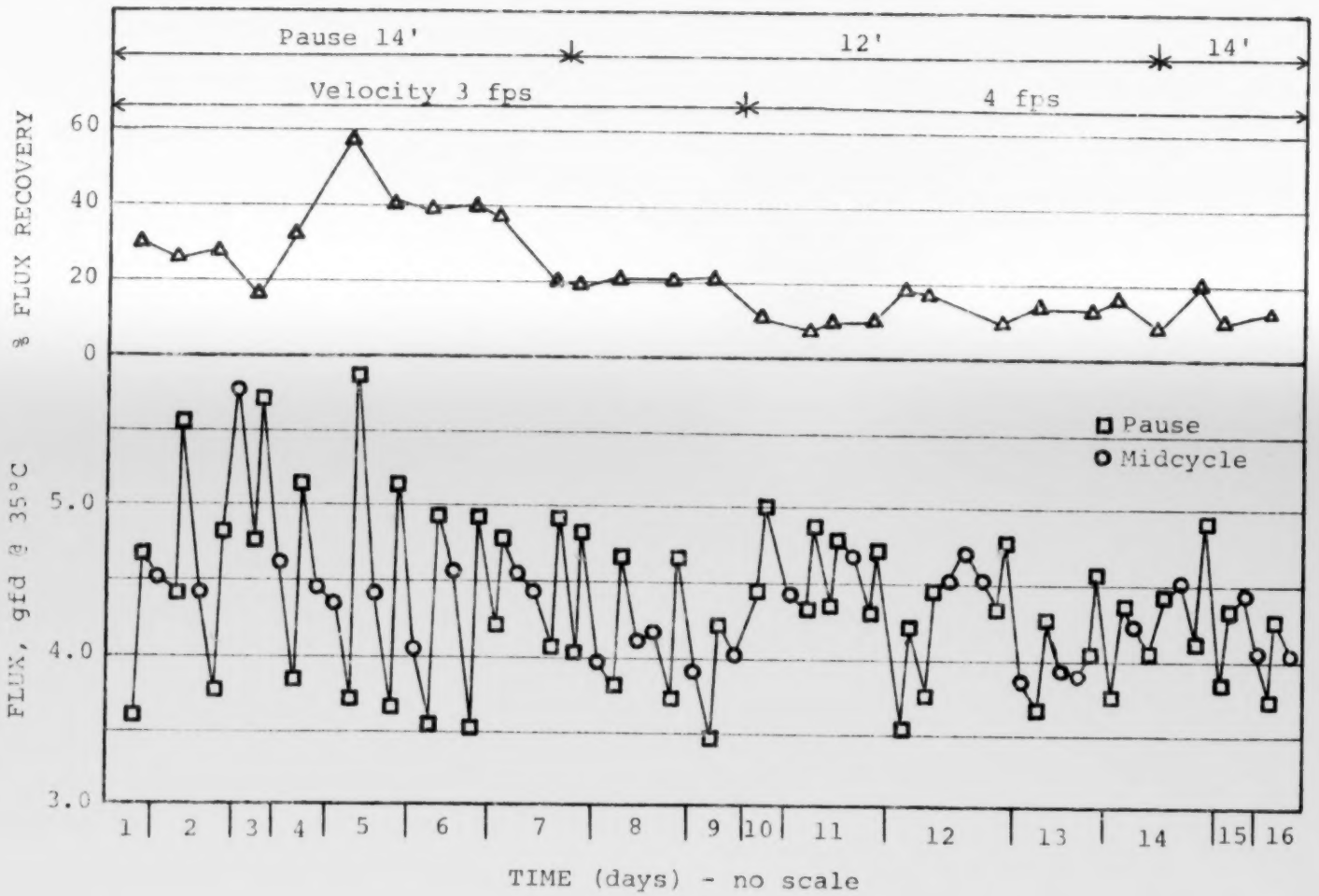


Figure 10. FOULING TEST AT 9 PERCENT FEED SOLIDS

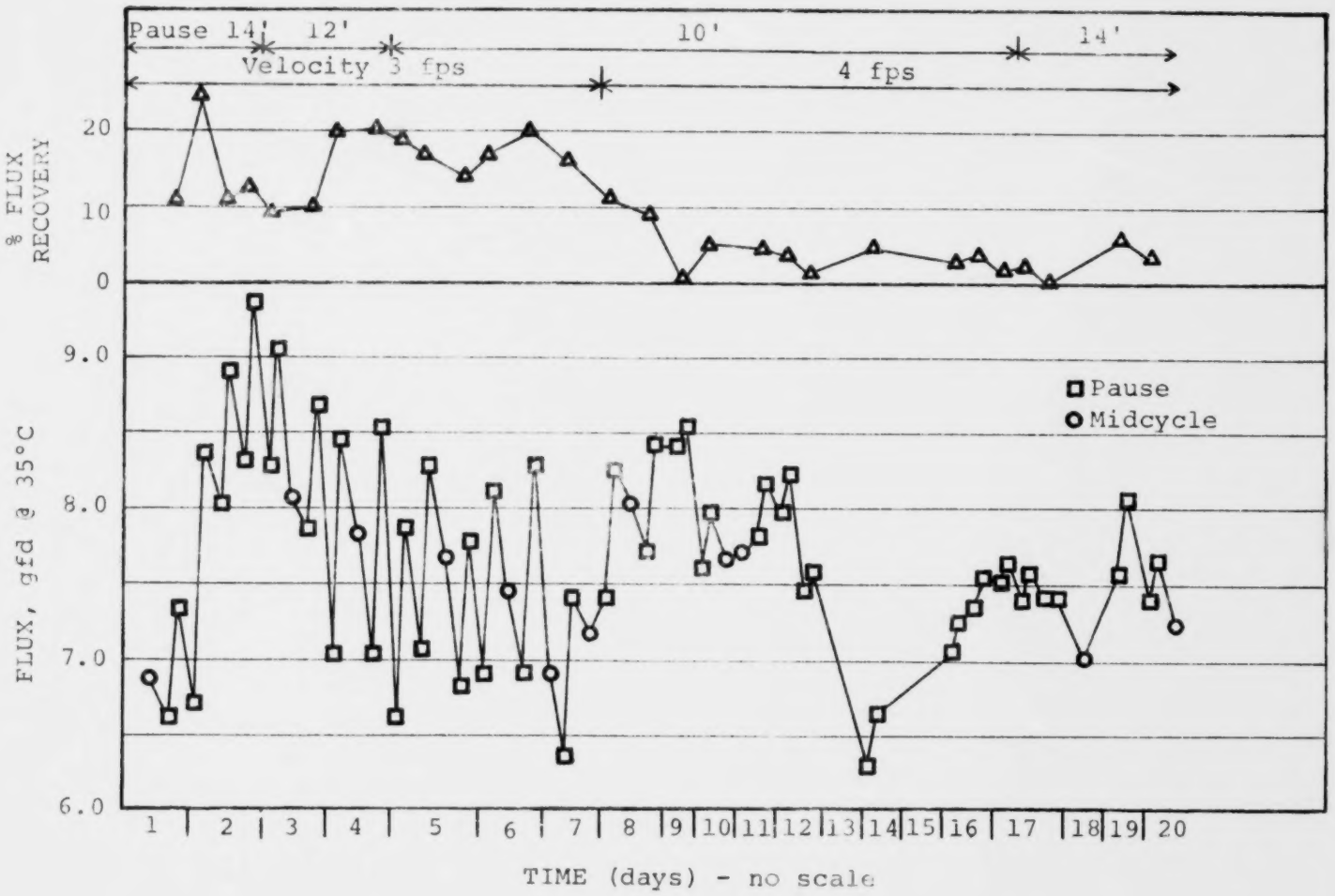


Figure 11. FOULING TEST AT 1.5 PERCENT FEED SOLIDS

Both figures include a plot of the percent flux recovery, which is defined as the percentage by which the flux rate recovers over a pause cycle. It had long been observed that this percentage was greater as fouling proceeded. During the pause trials, this factor became useful in judging the degree of temporary fouling that occurred in each cycle.

It has been observed that the optimum duration of the pause cycle varies little, if any, with the concentration of dissolved solids and suspended solids. A correlative observation is that percentage flux decay over a cycle varies little with concentration.

The experience with the pilot plants has indicated that the minimum pause cycle is eight minutes for total cycles of one hour, ten minutes for an hour-and-a-half, and twelve minutes for two hours. This corresponds to 13, 11, and 10 percent of the total operating time.

e. Minimum Velocity

Several brief tests were made to ascertain the minimum velocity required. In addition, three long runs were made in which velocity was one of the variable conditions. The two open half-inch tubular units were utilized in these tests. The minimum velocity in one unit was evidently about 4 feet per second, and in the other about 3.5 feet per second. Since these units were run under virtually identical conditions, the difference was attributed to turbulence; the unit tolerating a lower velocity contained a significant constriction at each 180° turn.

One unit was utilized for minimum velocity tests (in conjunction with the above pause tests) at both high and low feed concentrations. The minimum velocity was not significantly greater for higher concentrations.

In performing the pause and velocity tests, it was noticed that the pressure drop across the modules increased slightly (approximately 5 percent) as the unit became fouled. Apparently the reduced water removal in the initial modules resulted in a greater volume through the terminal modules, thus increasing the pressure drop.

Velocity tests per se were not performed with the tubular unit which contained turbulence promoters. Some velocity testing was performed on the unit with spiral-wound modules, but the results were inconclusive because of many processing problems. Toward the completion of testing on the latter unit, a modification in one section resulted in a velocity of about 5.0 feet per second as opposed to approximately 2.5 feet per second in the remainder of the sections. The absence of fouling in the higher velocity modules was evident.

f. Osmotic Water Requirements

The requirement for available water to be drawn back by osmosis during a pause cycle was not evident in our early experience with reverse osmosis tubes in a shroud. As we experimented with a unit which had no reservoir of product water adjacent to the membrane but did have transparent discharge lines, we observed the rapid drawback of air during the pause cycle. Theorizing that the evident osmotic driving force would be effective in lifting fouling from the membrane surface, the product water discharge line was submerged in a bucket. This permitted the return of permeate to the membrane. It resulted in a recovery in flux rate over a pause that was double the amount of recovery before the water was available. At that time these membranes had several hundred hours exposure. When the same unit was refitted with new membranes, it was found that more than four times as much water was returned. Evidently, the membrane backing remained more elastic and open to flow. The water availability also resulted in a reduction of the initial flux loss that occurs when new membranes are first exposed to the waste waters.

These results encouraged the vendor to modify half the modules to discharge at both ends, thus reducing the path both for permeate discharge and for the return of permeate during the pause. These double-ended modules, which had been exposed to our feed for over three hundred hours, immediately demonstrated a 20 percent increase in flux rate over the unmodified modules. This regained productivity continued in the ensuing months regardless of process variations. The volumes of water drawn back during a pause cycle were measured and reflected the improved return path developed by providing permeate connections at both ends of the module. It was also observed that the effect of water availability was more noticeable

during low-velocity trials when conditions for increased fouling were optimum.

Approximately 1700 hours later, the remaining modules on this unit were modified to discharge on both ends. The productivity of these modules slowly improved to within five percent of the flux rate of the modules that were earlier modified.

Since this one particular unit had little water adjacent to the membranes and had to draw it from the reservoir, it was possible to measure the quantities under varying conditions. During a fourteen-minute pause while running at low concentration (about 1 percent dissolved solids), the unit drew back about 10 cc per square foot of membrane surface. At high concentration (about 9 percent), the drawback was about 70 cc per square foot, approximately reflecting the ninefold increase in osmotic pressure. The rate of drawback was high immediately upon depressurizing and tapered off during the total pause time. The total volume increased slightly when the unit was being deliberately fouled. The operating velocity seemed to have no effect on the volume drawn back unless the velocity bordered the limit for fouling.

Tests were made with a dye in the product water which showed that the configuration of the piping is important; the returning water preferentially takes the least constricted route.

Some brief tests early in the program with the spiral-wound modules indicated that they drew back about 7 cc per square foot of membrane surface when the feed contained 1 percent dissolved solids.

Some volume return measurements were attempted with the second tubular unit (without turbulence promoters) but poor product water connections resulted in air being drawn into the piping. This unit had no flux difficulty, however, because the pressure tubes were within a flooded shroud.

One tubular unit, provided with turbulence promoters, was not flooded initially. A few modules were modified to flood the shroud. This resulted in a 7 percent improvement in the flux recovery during a manual pause, as opposed to nonflooded modules. This unit had no regular pause cycle and the flux rate deteriorated greatly. After 467 hours of operation, the entire unit (including flooded modules) had lost

36 percent of the flux rate while the flooded modules lost less than 5 percent. Later this unit was modified to have about 40 percent of the modules flooded. After further operation, the flux rate of the flooded modules was 18 percent greater than those not flooded.

This unit was then modified to incorporate a regular pause cycle, and the effect of flooding was less noticeable. After stabilized operations with proper depressurization, the productivity of the flooded modules was 8 percent greater than that of the non-flooded modules.

g. Number of Modules in Series

The measurement of the flux rate of the individual modules comprising a unit can determine variability, fouling, etc. During the pilot phase of this program, one vendor requested the measurement of individual modules during each of the many specific trials. Also, since the tests included trials on city water of low dissolved solids, there was an opportunity to compare modules with a standard fluid.

Each module in a group connected in series will perform differently from the previous module in the series since the pressure will be lower and the feed stream will contain a higher concentration of solids; thus, the flux rate of successive modules will drop. As large quantities of individual module data were acquired, it was realized that flux losses were disproportionate to any change in pressure or dissolved solids. This was noted even where the pause cycle was adequate and the velocity was high (see Figure 12).

The manufacture of membranes is known to result in variable performance from module to module; hence, the measurement of each module using city water produces a standard by which to reference later performance. These standard tests were performed at 500 psi inlet pressure and 3.3 feet per second velocity. Under the same conditions, the measurement of individual modules while operating with waste water feed showed a characteristic break in the flux plot. Figure 13 illustrates the variation in flux rate with reference to the module position on the same modules operating with both feeds.

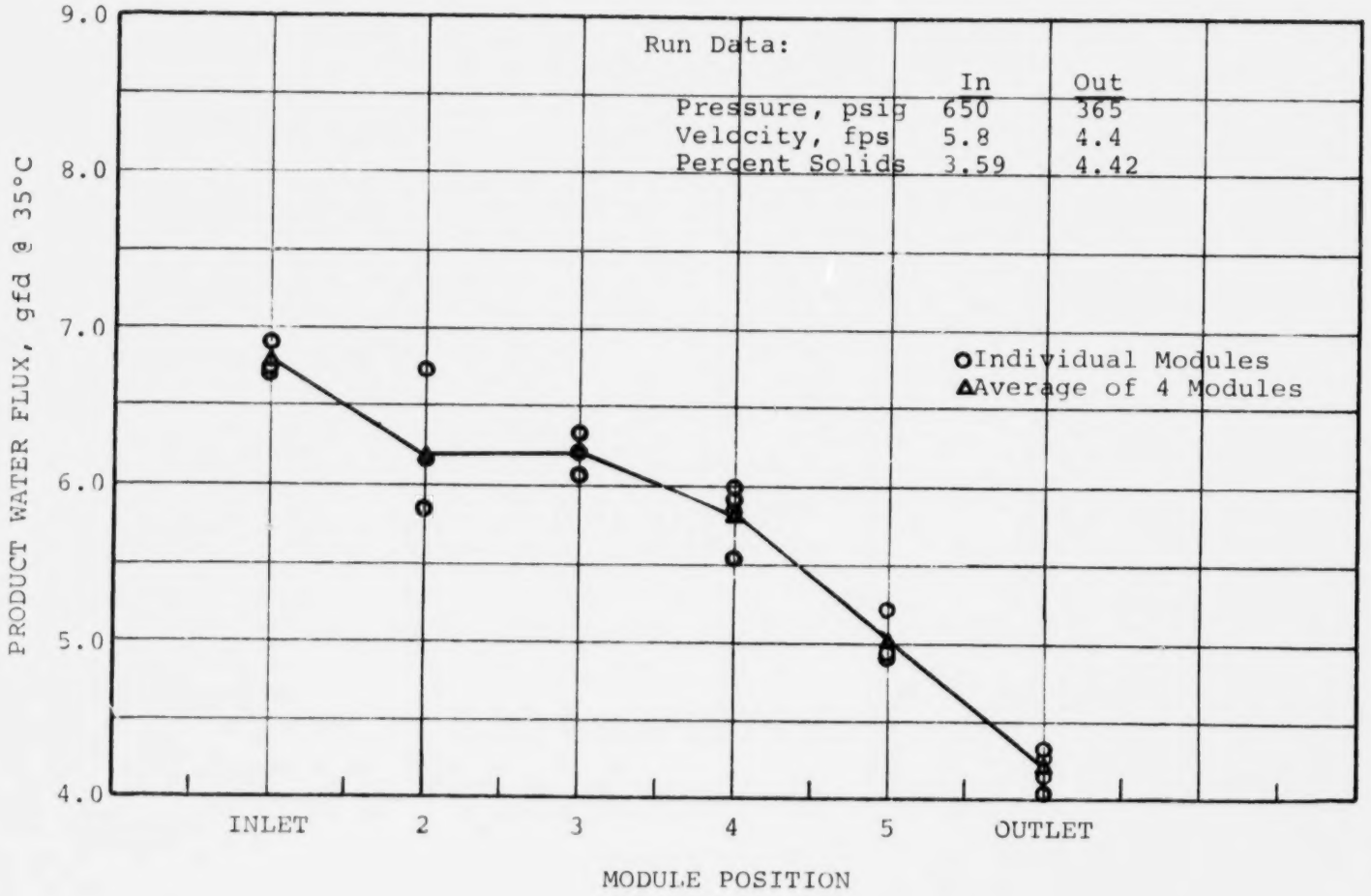


Figure 12. TYPICAL INDIVIDUAL MODULE FLUX RATES

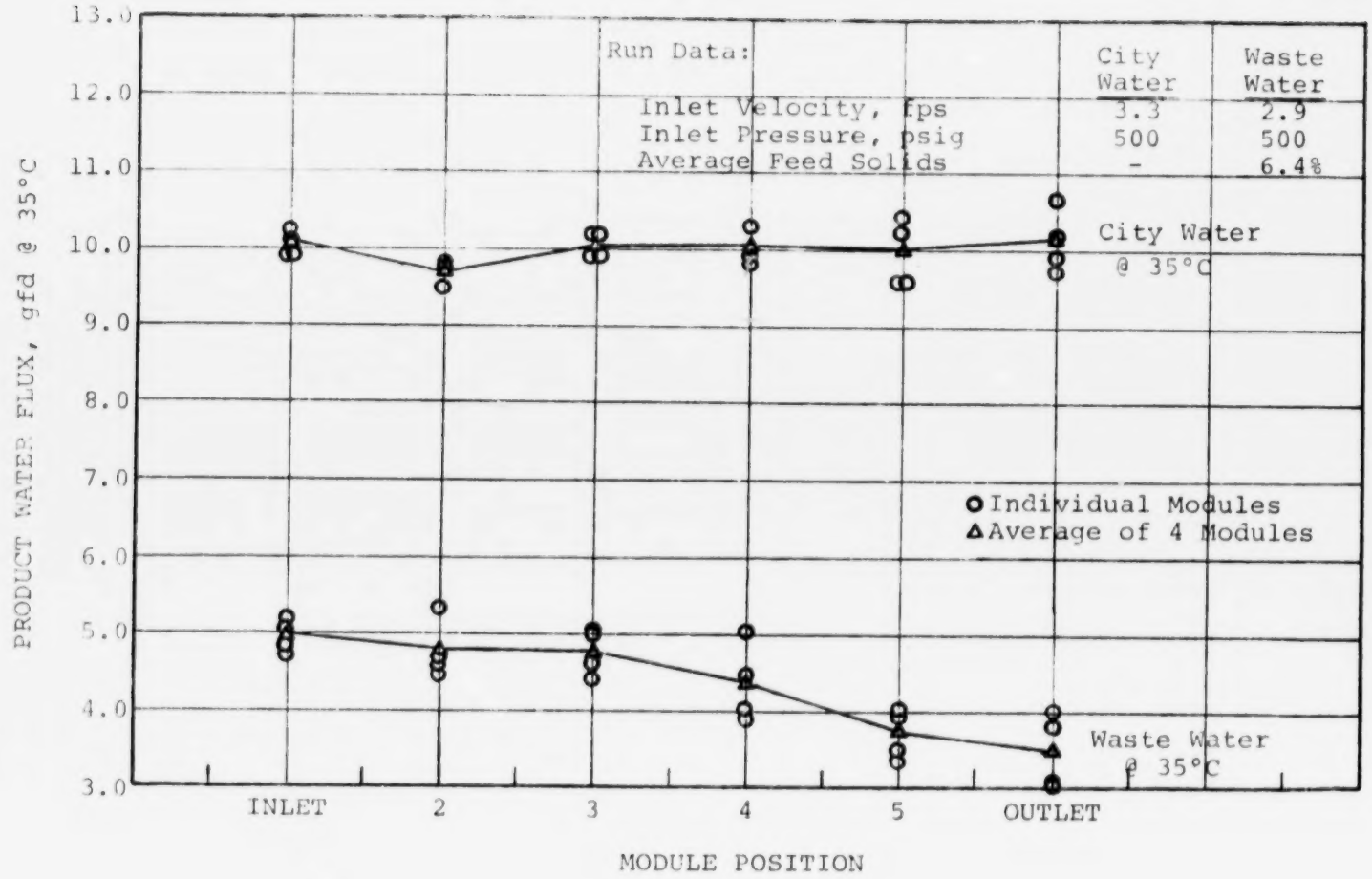


Figure 13. WASTE WATER VS. CITY WATER FLUX RATES

The tests on this particular unit included three major variables--pressure at two levels, three different inlet velocities, and five feed concentrations. The latter were very difficult to control, and any analysis of data requires grouping of concentration ranges. To simplify plotting, thirty tests were grouped by velocity and pressure; the feed solids concentration of individual runs was disregarded. A flux rate for each module position was computed by averaging the several results for the particular module. These six charts are illustrated in Figures 14, 15, and 16. Generally, the contour of these plots indicates that after about the third or fourth module in series, the flux rate shows more decay. One unusual feature noted in the individual tests as well as Figure 14 was that the first module in series when operating at 650 psi and 3 fps had a lower flux rate than the second module.

The unusual "S" curve often noted led to a comparison of two runs, utilizing the discharge conditions of one run as the inlet conditions for a second run. Figure 17 illustrates the inconsistency; the two plots could be expected to align reasonably well. To produce more information, one of the rows (of six modules in series) in the unit was modified to permit the measurement of pressure as well as feed solids at each module. Figures 18 and 19 illustrate the change in performance with position.

It was theorized that the plot of flux vs. average solids could be deceptive if the lower pressure in modules 5 and 6 resulted in a lower flux. Similarly, the increasing solids effect in modules 5 and 6 could be influencing a plot of flux vs. average pressure. Hence, an empirical number was derived by multiplying the average pressure and average solids content for each module, and this product was plotted versus the flux (see Figure 20). Again, it may be seen that the last two modules perform quite differently.

The many test results implied both that fewer modules in series was desirable and that the pilot data could not be merely applied to a production plant design without some verification that fewer modules in a short series behaved in the same manner as the first few modules in a longer series. Thus a brief test was made in which the unit was operated with only three modules in series. After an initial set of data was obtained, the feed conditions for the second run were modified to simulate the discharge conditions

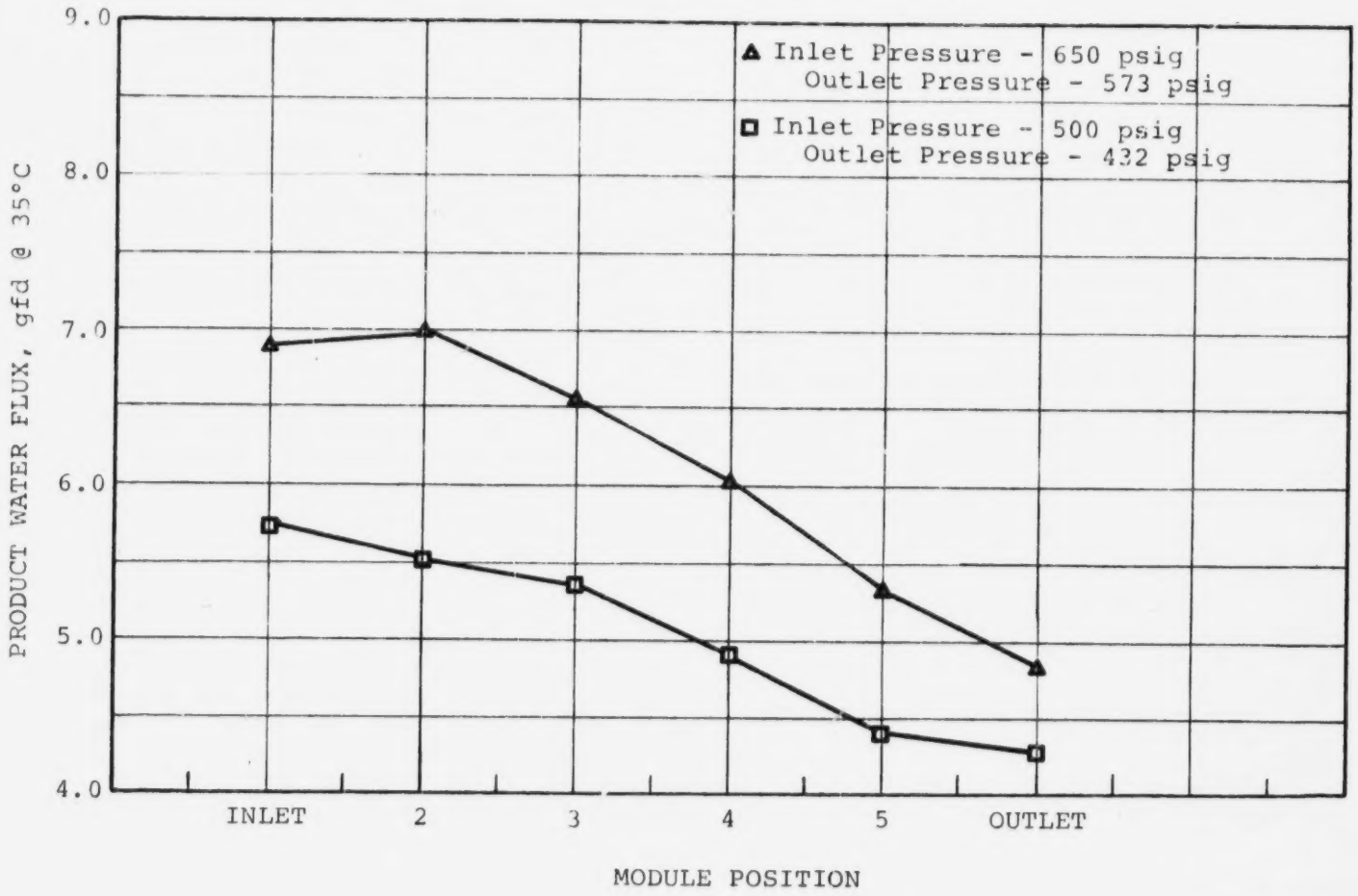


Figure 14. INDIVIDUAL MODULE FLUX RATES AT 3 FPS VELOCITY

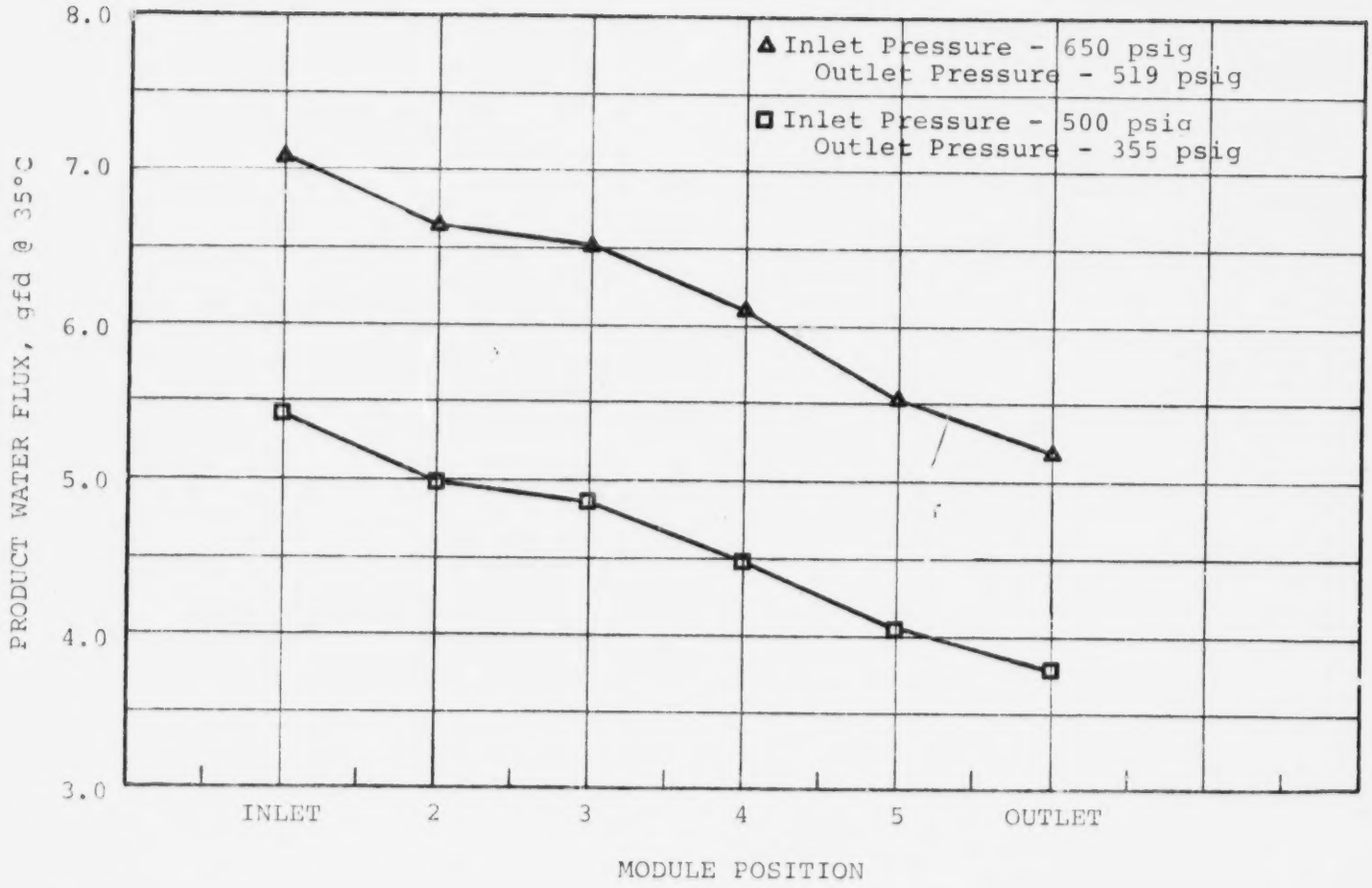


Figure 15. INDIVIDUAL MODULE FLUX RATES AT 4 FPS VELOCITY

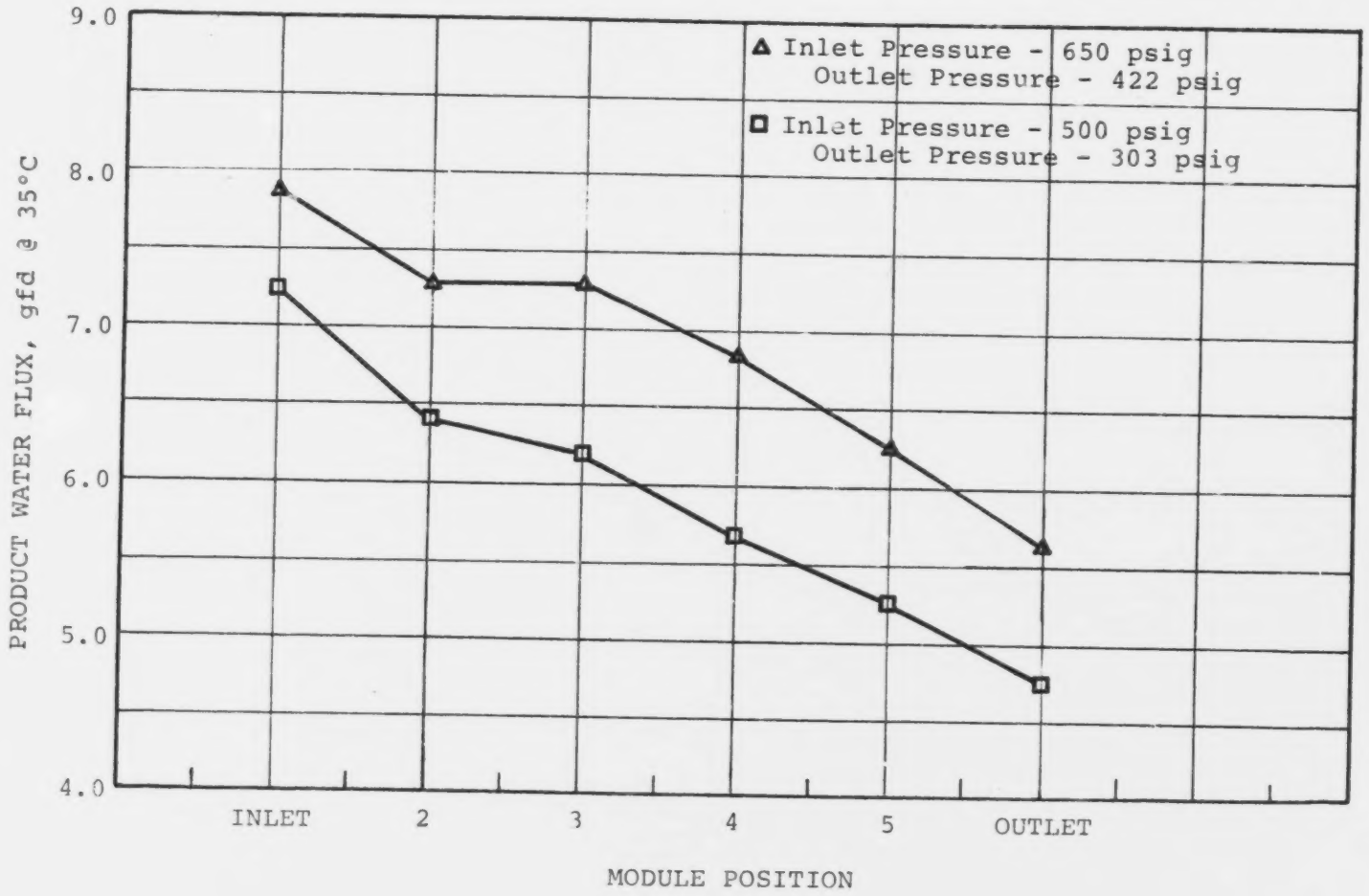


Figure 16. INDIVIDUAL MODULE FLUX RATES AT 5 FPS VELOCITY

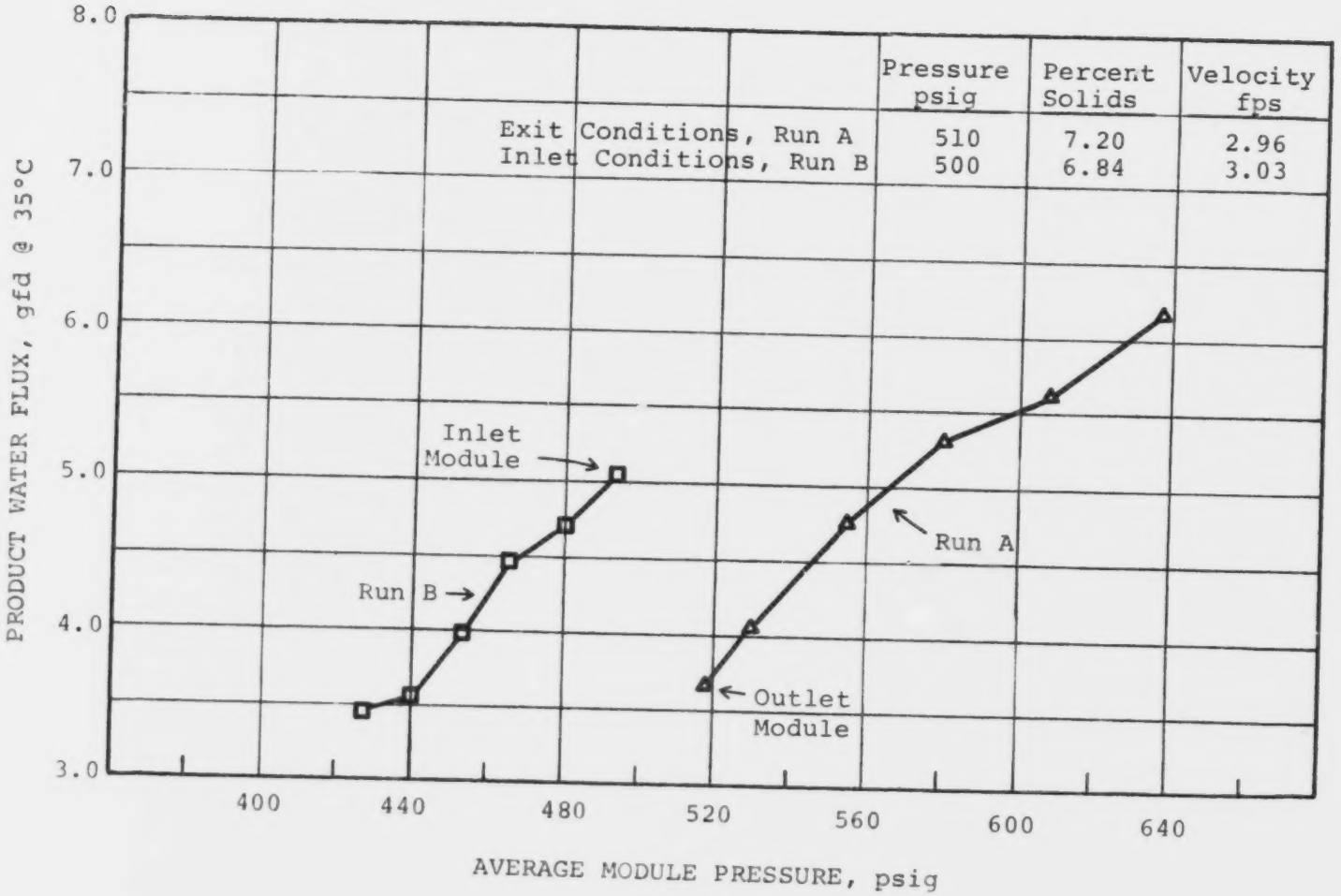


Figure 17. PRESSURE VS. FLUX, COMPARISON OF TWO RUNS

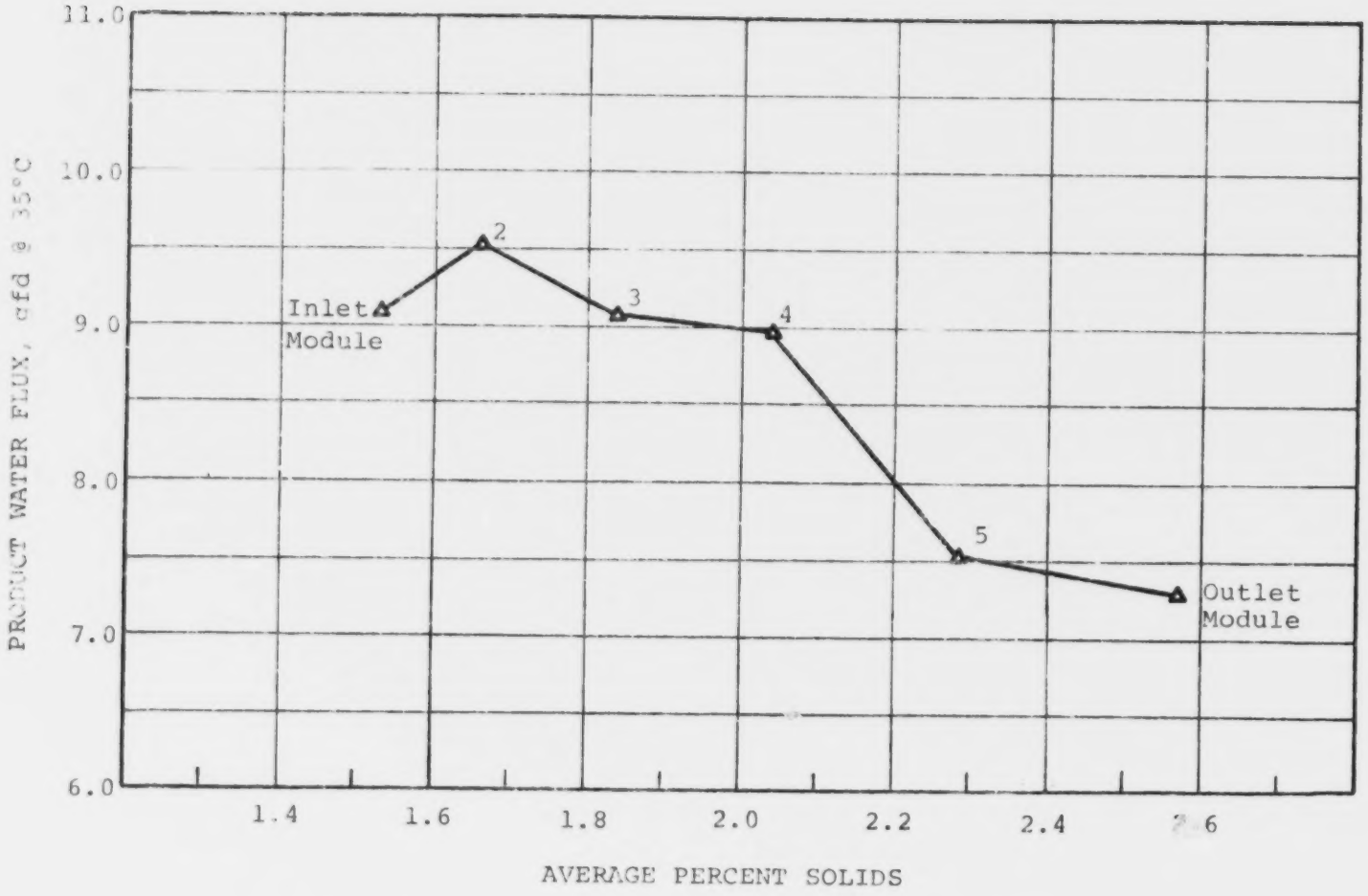


Figure 18. MEASURED SOLIDS VS. FLUX FOR MODULES IN SERIES

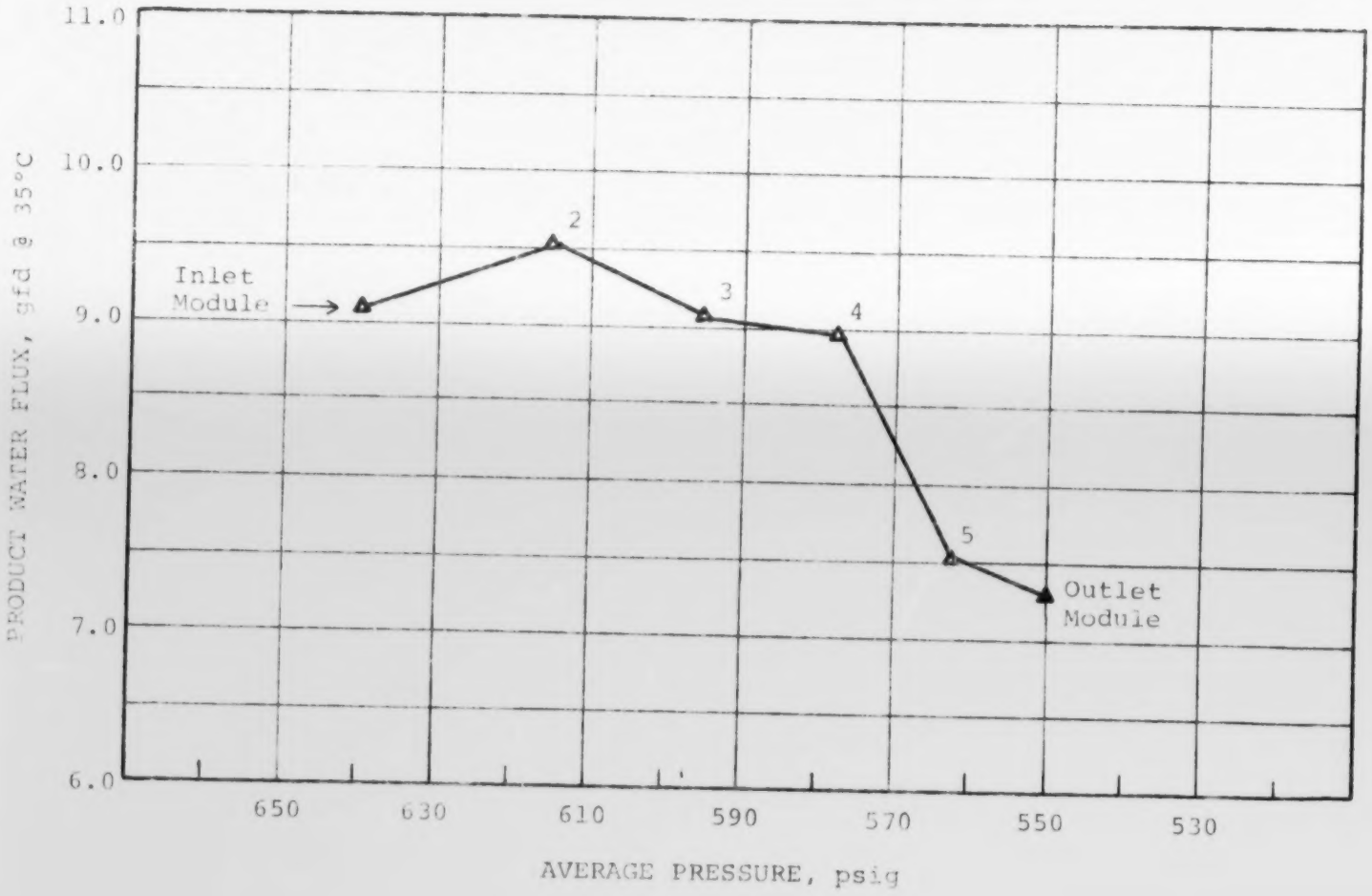


Figure 19. MEASURED PRESSURE VS. FLUX FOR MODULES IN SERIES

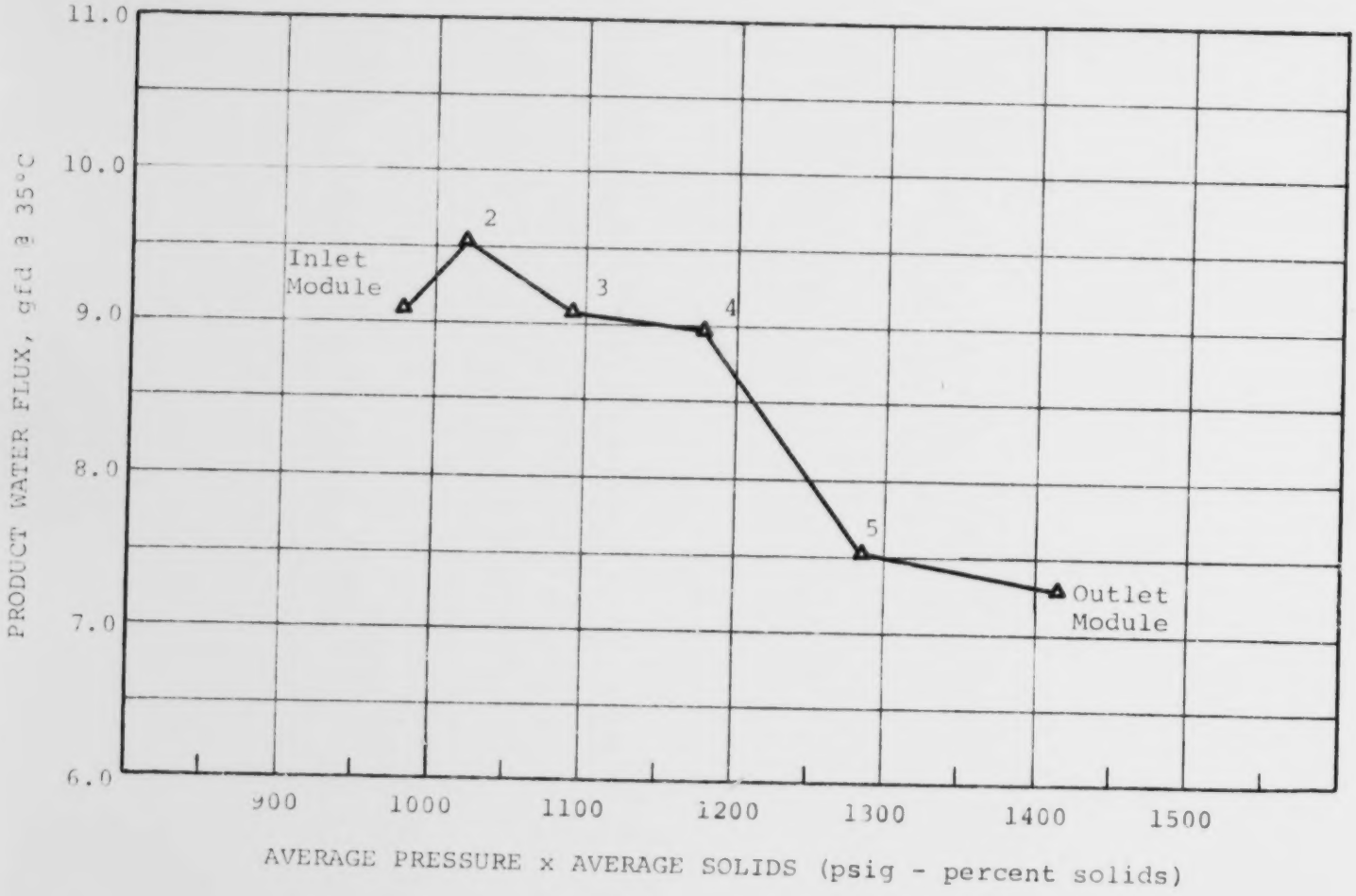


Figure 20. PRESSURE-SOLIDS FACTOR VS. FLUX FOR MODULES IN SERIES

of the previous run. The results, shown in Figure 21, may be compared with Figure 17.

h. Removal of Fouling

During our early experience with reverse osmosis, the processing techniques for preventing fouling were not understood; later, heavy fouling occurred because of equipment limitations. It has been our general experience that after an extended period, fouling is very difficult to remove. The mill practice for removing fines accumulations from process equipment such as heat exchangers is to wash with a strong caustic solution, which is, of course, not compatible with cellulose acetate membranes. Several attempts were made to remove fouling using neutralized solutions of enzyme detergent, which had only a limited effect. Allowing bacterial action to take place by shutting a unit down for extended periods with feed against the membrane also resulted in only limited improvement. Reversing the flow past the membranes for short periods had little effect. Back-flushing with feed, clear water, etc., did not improve the membrane productivity appreciably, although it helped remove accumulations at sites other than the membrane. Long shutdowns with clean water did not produce much improvement.

The one technique that has proven effective although slow is to operate with adequate depressurization cycles and during the operating cycle to increase the velocity 10-15 percent above normal. It is suspected that the heavy, stable fouling is eroded away with time.

Occasionally, light fouling has been both physically observed as well as reflected in the operating results. This has occurred despite operating with an adequate velocity, pause cycle, etc., that previously had effectively controlled the fouling. After a period of time, the fouling would disappear. No explanation has been found for this.

## Process Results

The productivity of the membrane (flux rate) was similar to that experienced previously on our feed. Typical curves of flux vs. average feed concentration from two different units are illustrated in Figures 22 and 23. The curves are not identical, of course, because of different pressure ranges, equipment configuration, etc.

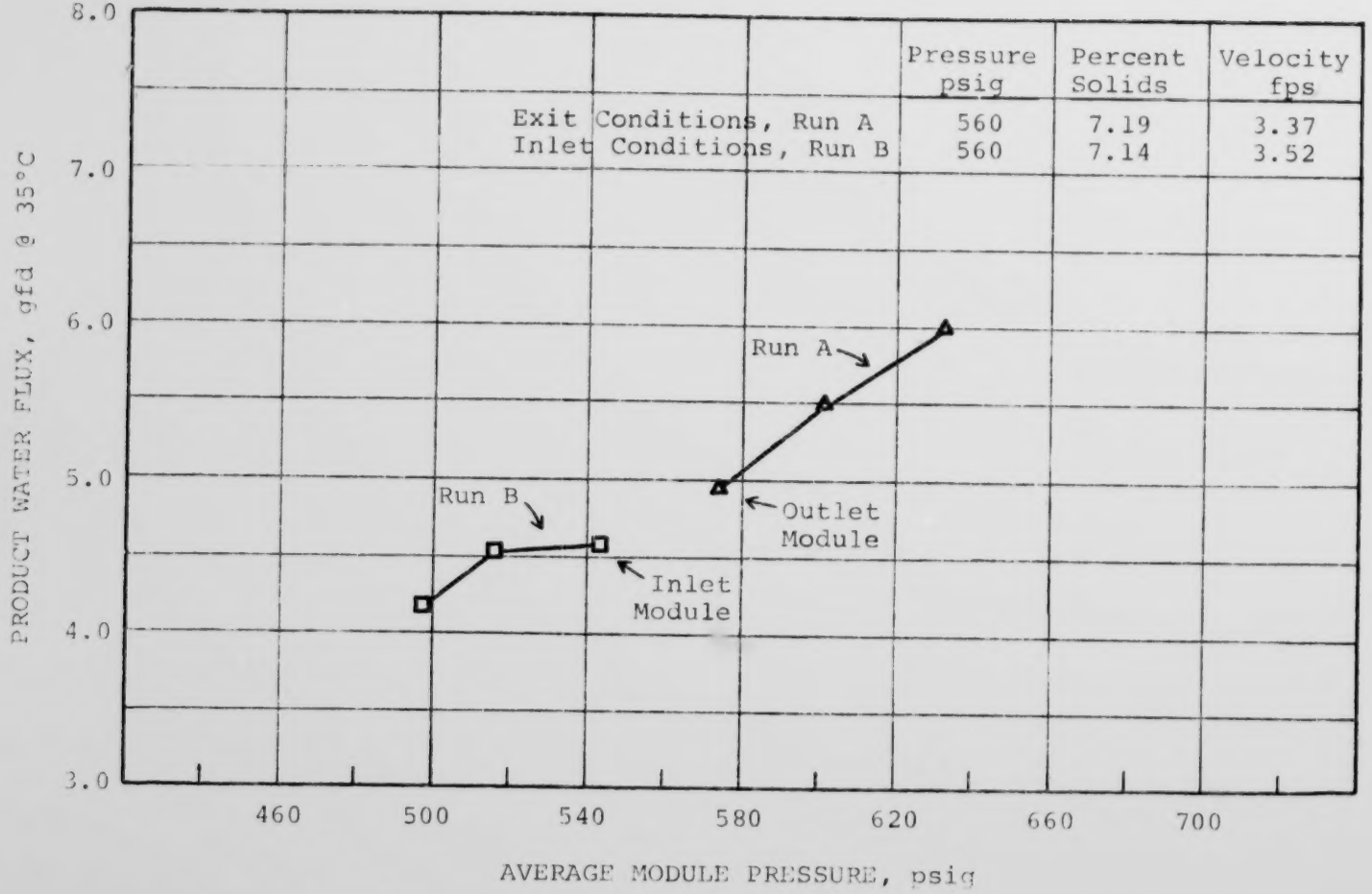


Figure 21. PRESSURE VS. FLUX, COMPARISON OF TWO RUNS

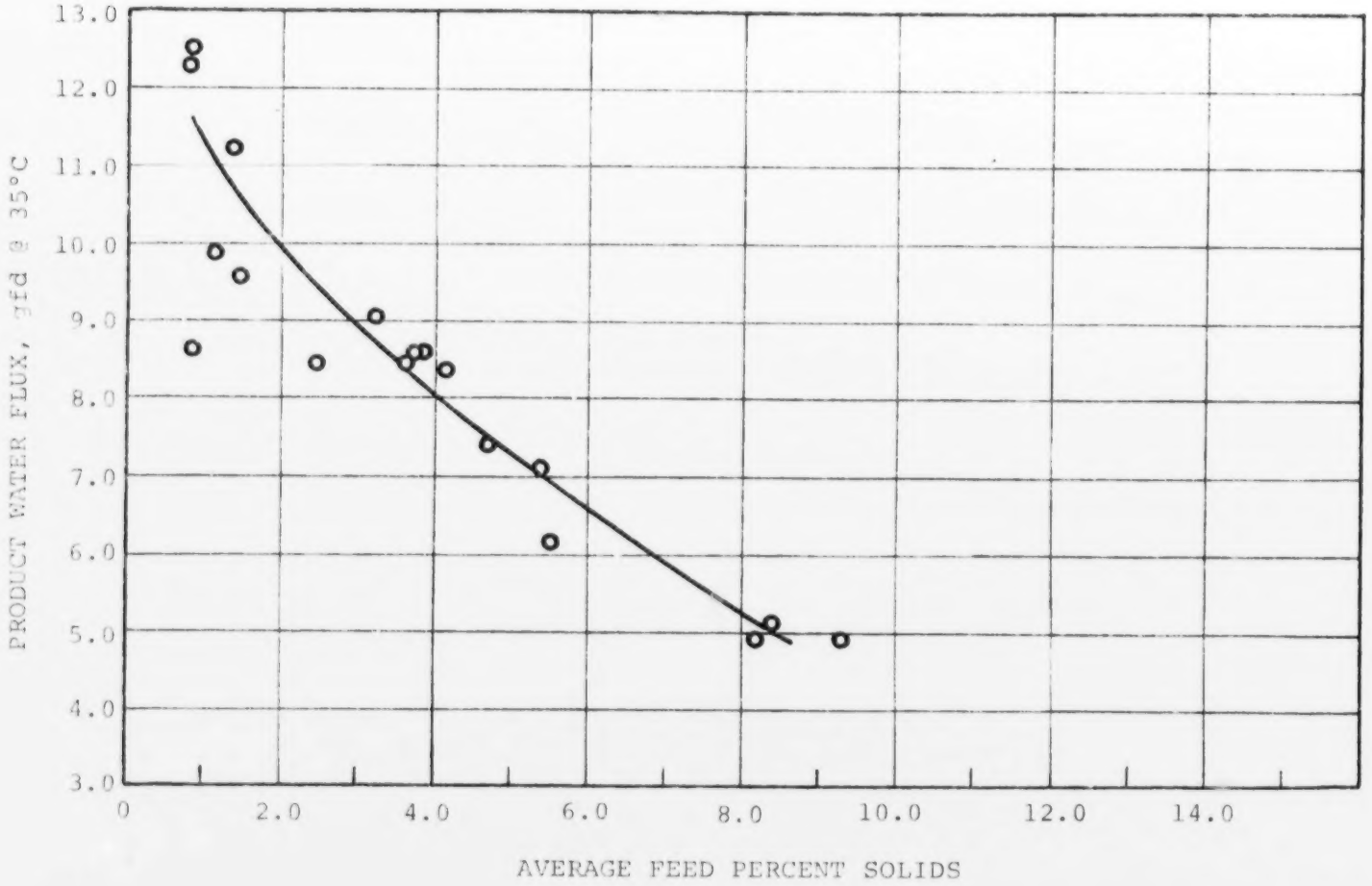


Figure 22. FLUX RATE VS. CONCENTRATION OF FEED (UNIT X)

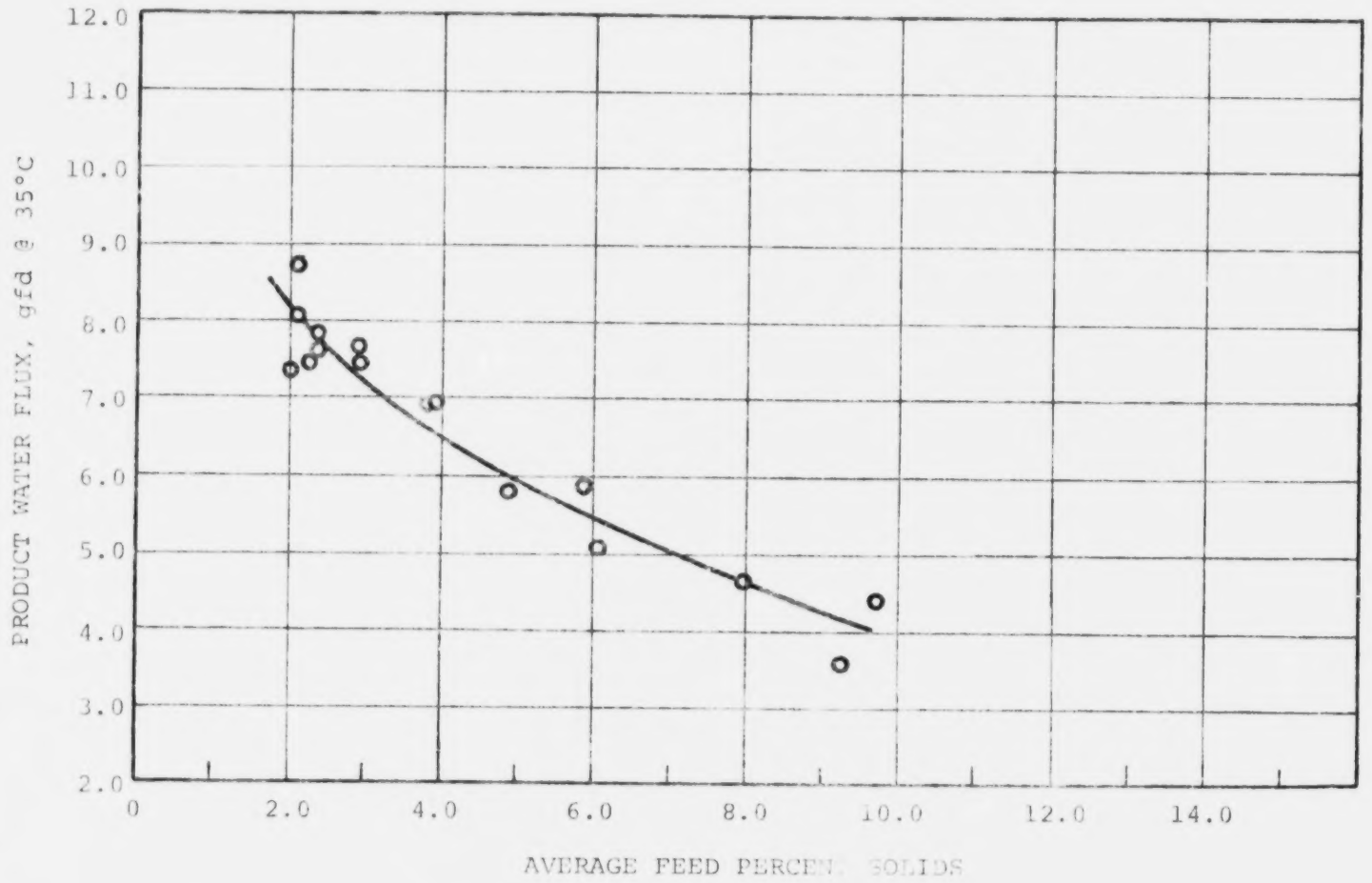


Figure 23. FLUX RATE VS. CONCENTRATION OF FEED (UNIT Y)

The osmotic pressure of the waste stream was measured using one of the pilot plants. The technique involved blocking the product water channels and measuring the pressure on the back side of the membrane. This pressure subtracted from the operating (feed) pressure yielded the osmotic pressure. In this test, the osmotic pressure averaged about 31 psi for each percent soluble solids in the feed.

The effect of temperature on membrane productivity (flux rate) was found to be 3.0 percent per °C in the range of 5-25°C, and 2.3 percent in the range of 25-40°C (using city water as the test fluid). These corrections were applied to all the data taken during the trial period.

The ability of the membranes to reject dissolved solids was found to be excellent. Rejection has been calculated on total quantities and not on concentration. The lowest rejection of soluble solids from all samples was 99.37 percent; the lowest sodium rejection was 99.48 percent. One sample for $BOD_5$ resulted in a rejection of 97.44 percent; all other $BOD_5$ samples were greater than 98.25 percent.

The rejection of color as determined by a subjective optical comparison device is imprecise, but the lowest rejection encountered was 99.92 percent. The measurement of color using a spectrophotometer operating at the nominal wavelength of lignin yielded a lowest rejection of 99.67 percent.

The average rejections with highest and lowest readings experienced on each unit in these trials are listed in Table 7.

The percent rejection increased slightly with an increase in feed concentration, as would be expected in a recycle system. There was no evidence that the membrane performance declined with continued exposure. This is discussed later in the report.

The product water quality, as judged by the percent rejection, was excellent over the entire range of feed concentrations. Figure 24 illustrates the change in product water soluble solids as the average feed solids is increased. The average feed solids for each run is an average of the concentration in the feed and concentrate streams. Similarly, Figures 25, 26, and 27 illustrate the variation of product water sodium, biochemical oxygen demand ($BOD_5$), and color over the range of average feed concentrations.

Table 7

PERCENT REJECTIONS EXPERIENCED ON ALL UNITS

| Parameter | Units | | | |
|---|---|---|---|---|
| | American Standard | Aqua-Chem | Gulf | Havens |
| Soluble Solids | | | | |
| High | 99.86 | 99.92 | 99.99 | 99.93 |
| Average | 99.71 | 99.80 | 99.97 | 99.92 |
| Low | 99.37 | 99.45 | 99.92 | 99.71 |
| Sodium | | | | |
| High | 99.70 | 99.89 | 99.99 | 99.89 |
| Average | 99.54 | 99.66 | 99.95 | 99.79 |
| Low | 99.48 | 99.13 | 99.85 | 99.64 |
| $BOD_5$ | | | | |
| High | 99.03 | 99.82 | 99.97 | 99.77 |
| Average | 98.64 | 99.20 | 99.85 | 99.56 |
| Low | 98.26 | 97.44 | 99.64 | 99.12 |
| Color - Optical Comparator | | | | |
| High | 100.00 | 100.00 | 100.00 | 100.00 |
| Average | 99.99 | 99.99 | 100.00 | 100.00 |
| Low | 99.94 | 99.92 | 99.99 | 99.98 |
| Color - Spectrophotometer | | | | |
| High | 99.94 | 99.99 | 100.00 | 99.98 |
| Average | 99.85 | 99.91 | 99.98 | 99.94 |
| Low | 99.77 | 99.67 | 99.95 | 99.79 |

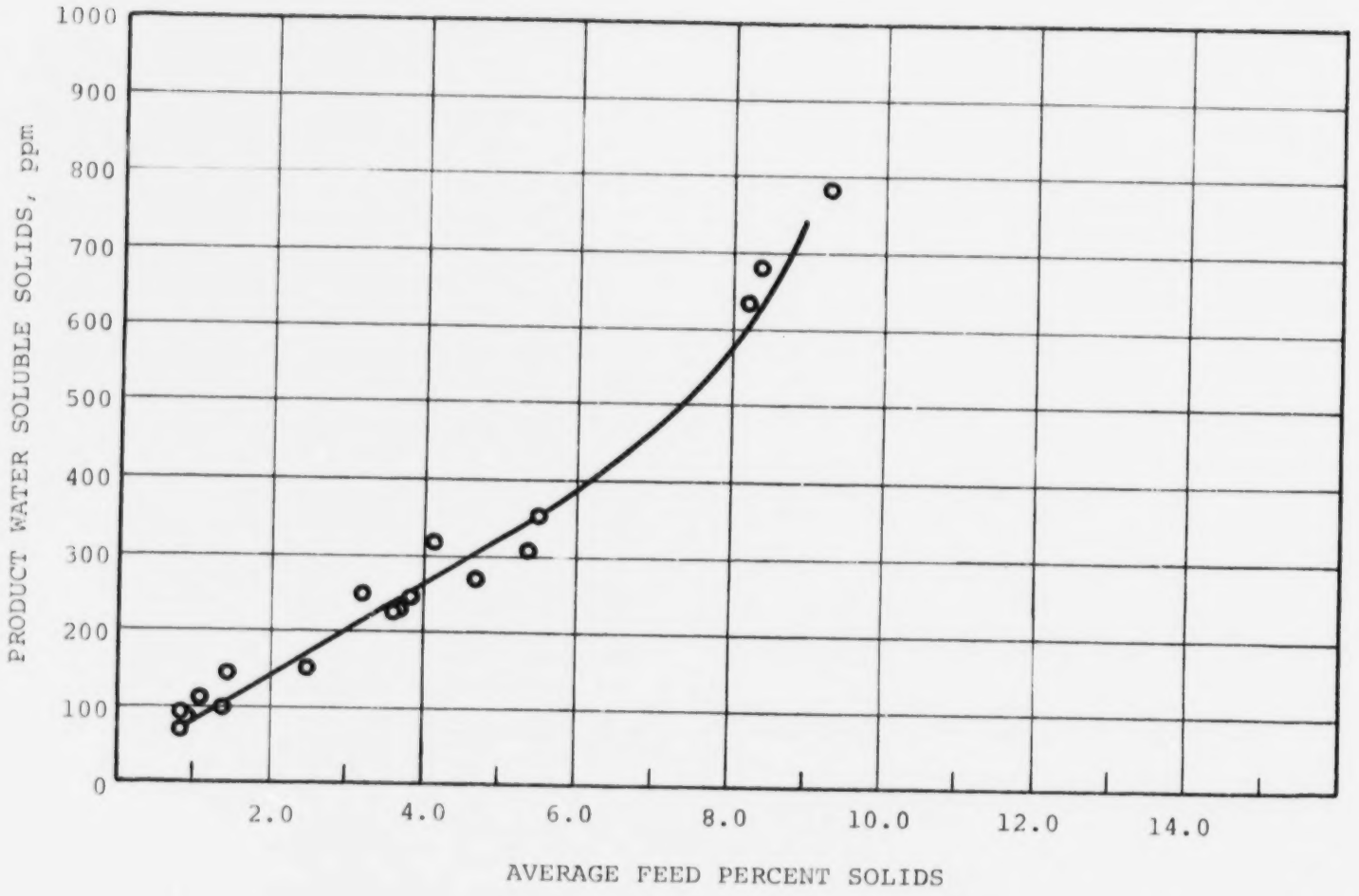


Figure 24. FEED SOLIDS VS. PRODUCT WATER SOLUBLE SOLIDS

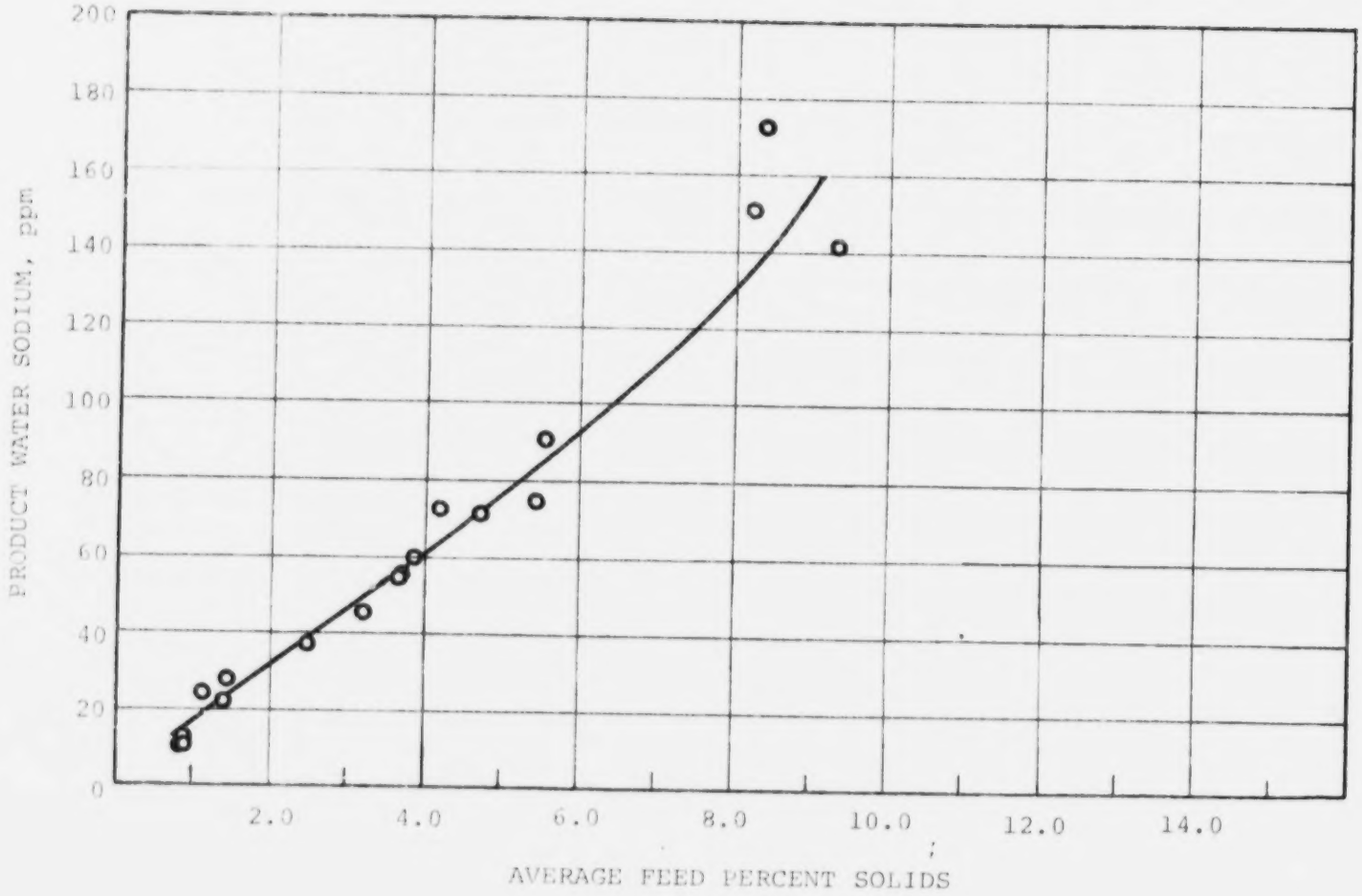


Figure 25. FEED SOLIDS VS. PRODUCT WATER SODIUM

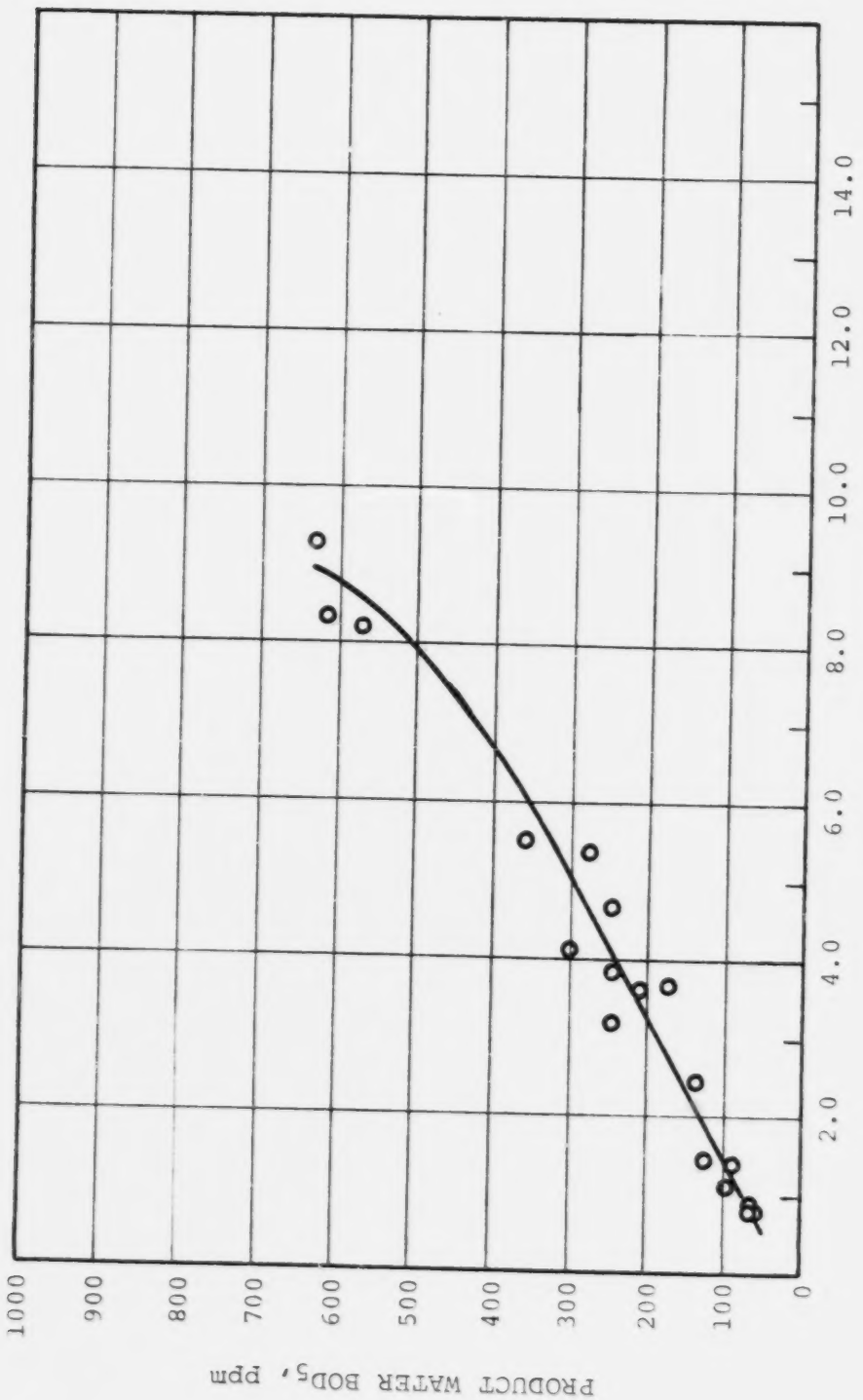


Figure 26. FEED SOLIDS VS. PRODUCT WATER $BOD_5$

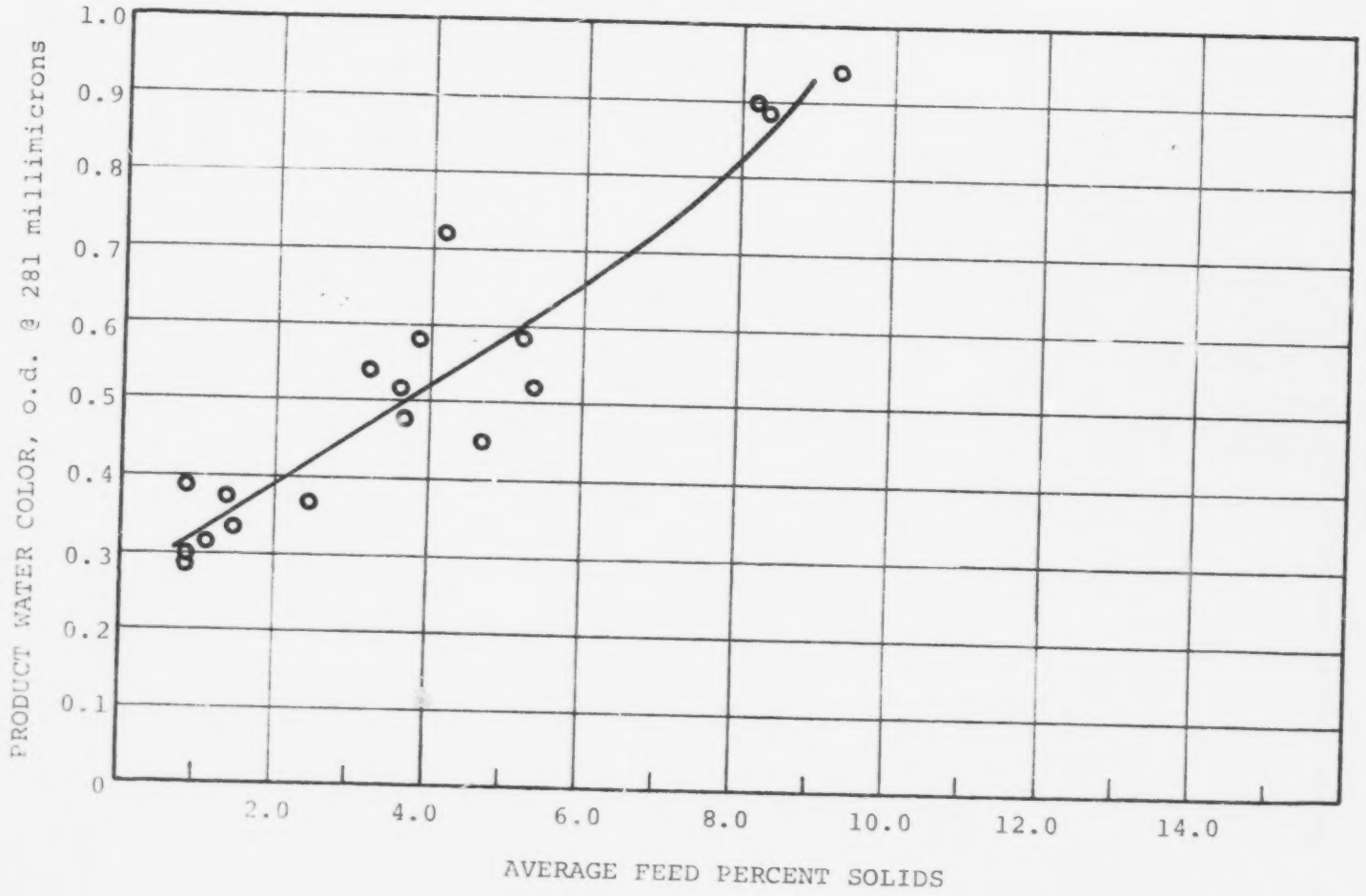


Figure 27. FEED SOLIDS VS. PRODUCT WATER COLOR

The criterion by which the total plant discharge is judged is the reduction of $BOD_5$. The efficacy of reverse osmosis in separating $BOD_5$ may be seen in Figure 28, which illustrates the variation in product water $BOD_5$ with the feed $BOD_5$ content.

The conductivity of the product water was measured throughout the trial runs in order to determine the relationship with $BOD_5$ content. Figure 29 shows this relationship determined from a total of 34 runs on two units.

It has been known from earlier studies that the primary constituent in the product water was sodium acetate; however, the nature and proportions of the several components had not been determined on samples taken from field units. Hence, samples were obtained from two runs--one in which the feed contained 3.02 percent solids, and the other 10.02 percent solids. The tests, performed by outside agencies, disclosed that there was little significant difference in the constituents dissolved in the product water. The solids in both product waters consisted of about 80 percent sodium acetate; and the total organic carbon was proportionate to the difference in dissolved solids.

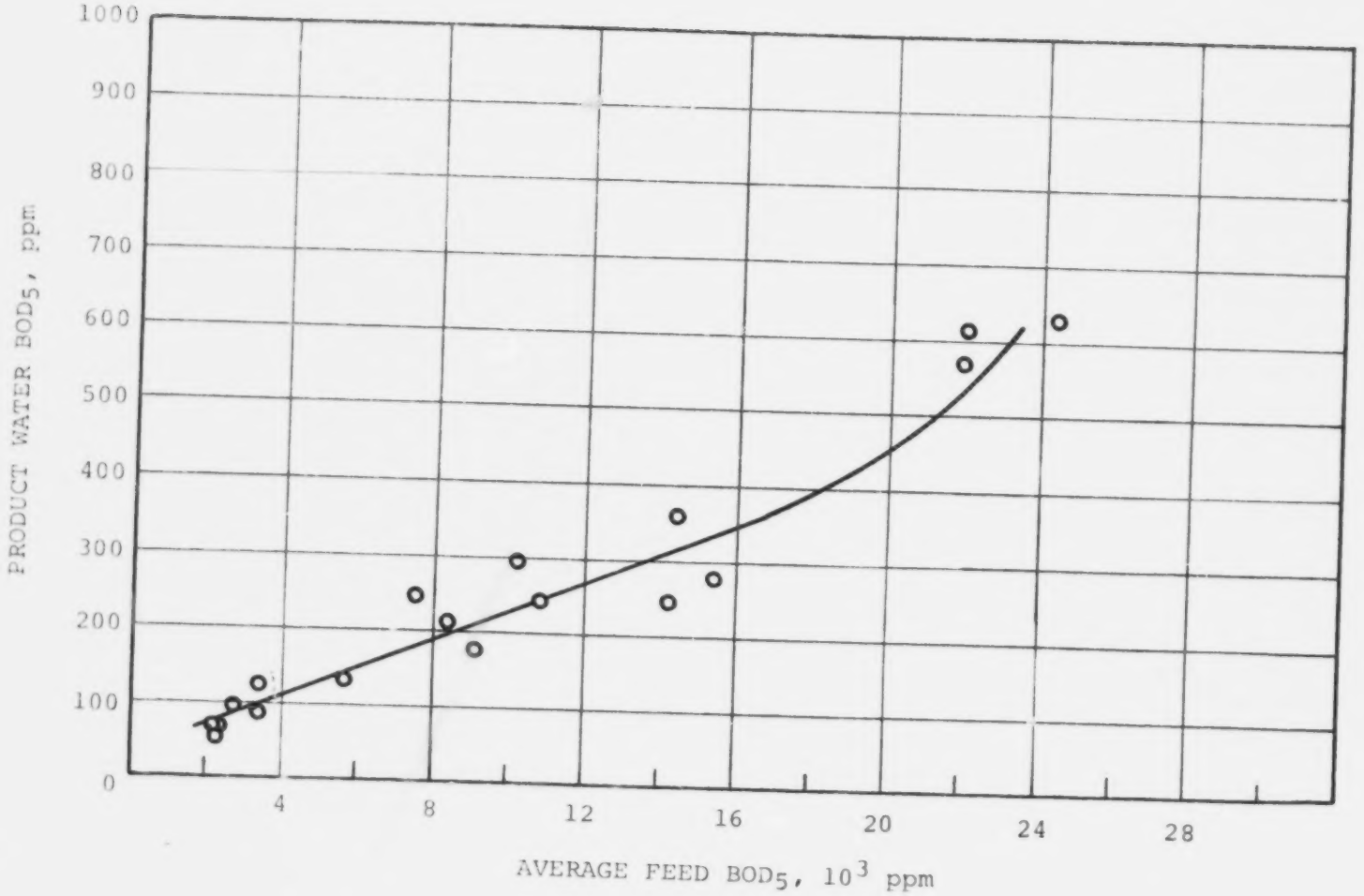


Figure 28. FEED $BOD_5$ VS. PRODUCT WATER $BOD_5$

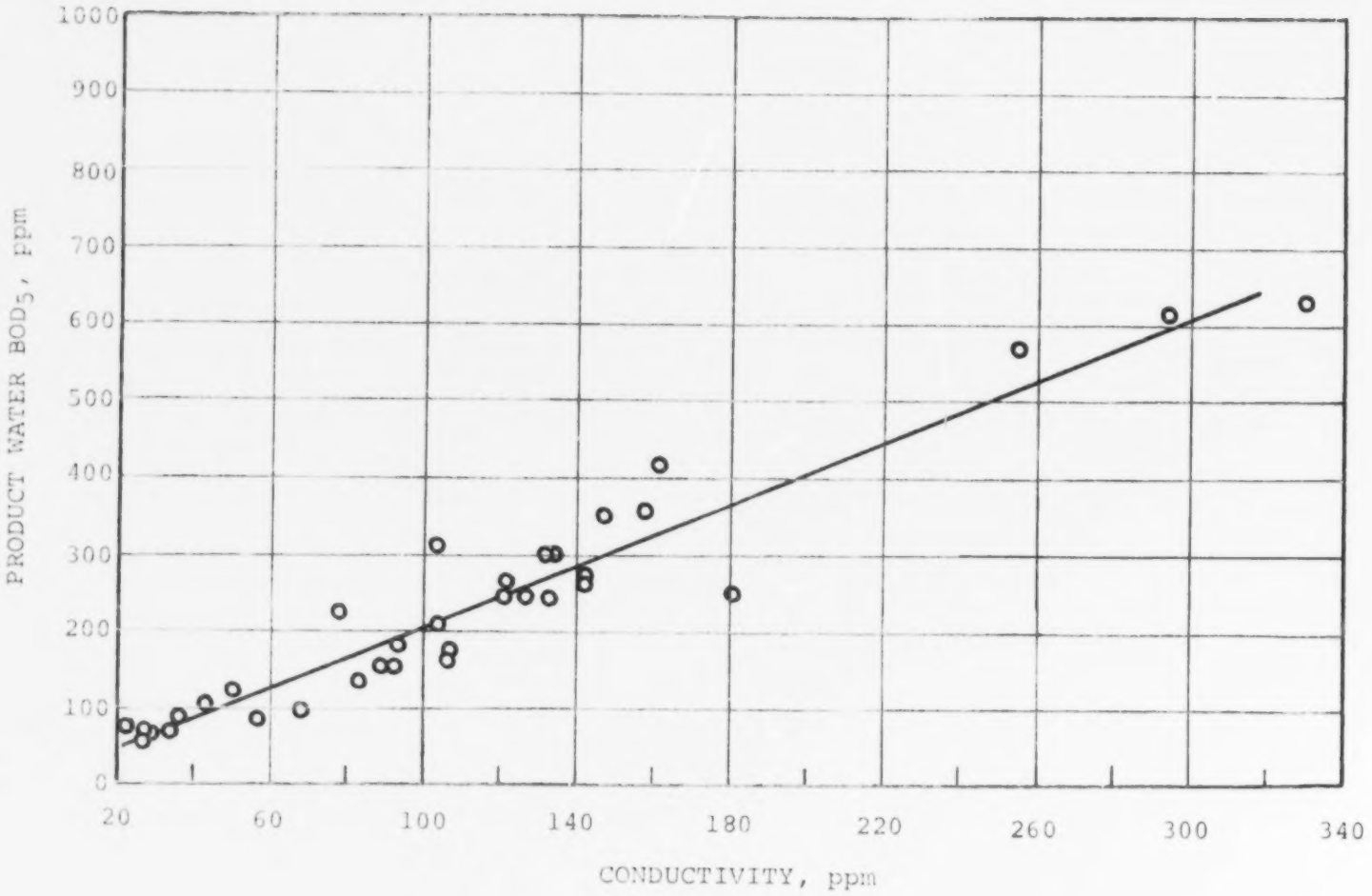


Figure 29. CONDUCTIVITY VS. PRODUCT WATER $BOD_5$

# SECTION IX

## DISCUSSION OF PROCESS INVESTIGATION

Three factors detracted from obtaining the maximum amount of information during these trials. First, the scope of the tests and intensive effort in a relatively short time interfered with the orderly development of the investigation. Second, mechanical difficulties with the pilot plant equipment interfered with the completion of tests. Third, the variability of the feed supply and the dynamic nature of the membrane process made precise control and experimentation difficult. Nonetheless, a large quantity of data was obtained from which many conclusions may be made.

The quantitative data, such as flux rate vs. feed solids, was sufficient for estimating the criteria for a production facility. The data were statistically analyzed, but it was found that there was no simple equation for most relationships.

It is concluded that allowance must be made in designing a production facility for loss of membrane productivity. The apparent permanent loss is approximately 20 percent. Ten percent is presumed to be caused by a reaction of the membrane to one or more constituents in the waste water feed. There is an additional 10 percent loss of productivity that is assumed to be the result of membrane compaction. This also must be considered a permanent loss since a production unit is expected to remain in operation virtually continuously.

It was determined that the process can easily produce a concentrated waste stream containing 10 percent dissolved solids, at which point conventional evaporation and combustion processes are feasible. The product water recovered was of excellent quality and is suitable for many process operations requiring clear water. All analyses on the product water indicated that there is little or no change in the proportion between the various dissolved constituents at different levels of concentration.

The data for product water $BOD_5$ and conductivity were statistically analyzed, and there is a strong correlation ($r = 0.96$) between these two properties. The use of conductivity for monitoring plant performance in terms of product water quality is warranted.

All evidence in the trials indicated that the number of modules in series is critical. There were indications of poor performance even when the discharge velocity from the last module in a long series was above what is considered to be the minimum velocity. It is concluded that the number of modules in series should be less than was utilized in the pilot phase. Such a reduction would require more staging and "pyramiding" to effect the necessary concentration, but the expense would be warranted. Performance variation between modules, which is characteristic in the membrane processing field, will result in irregular series flow conditions. The effect of such performance variations would be minimized by reducing the length of the fluid path before the flows are combined and redistributed for another stage.

One unexplained inconsistency noted in performing the tests was the lower flux rate that often occurred in the first module in series.

The major effort to define the techniques to prevent membrane fouling resulted in certain firm conclusions. The mechanical construction of the module must be such that there will be no membrane areas unexposed to high velocity. The minimum velocity identified for the waste water feed investigated is higher than previously reported and must be about four feet per second. Since the fouling is not primarily caused by concentration polarization, turbulence promoters are of little value.

Unless some preventive technique or better flux regenerative technique can be developed, a pausing cycle is required together with an opportunity for the return flow of product water. This cycle will result in an effective loss of 10 percent of the plant capacity at any given time. The requirement for routine depressurization will result in higher costs, not only for extra membrane surface area, but also for reliable control of the cycle. The pausing cycle determined by the trials is quite uniform over the range of concentrations. It is theorized that at higher concentrations the more dense fouling is lifted by the higher osmotic flow, and thus the same cycle may be used for all stages.

There must be an unobstructed path for the return of product water during the pause cycle. This path must extend to within the module structure up to the back side of the membrane support structure.

The fouling accumulates in a definite pattern that does not seem to be influenced by the concentration of the feed.

Fouling is not easily detected by one or two measurements of the flux rate since the membrane productivity is so sensitive to influences such as momentary changes in the feed concentration. The amount of flux recovered after a pause (percent flux recovery) is the most sensitive indication that fouling is occurring.

Fouling of the type experienced is not easily removed, particularly if allowed to continue. No special technique was found which readily removed accumulated fouling.

A final comment is necessary about the results of this investigation. It was found that there is an inter-dependency between the processing variables that has made it difficult to reach firm conclusions about any one variable. Better process definition will require extensive experience at steady conditions with a large, reliable unit.

## SECTION X

## SPECIAL PROCESSING - HIGH TEMPERATURES

During past investigations of reverse osmosis, it had been understood that the maximum temperature to which cellulose acetate membrane could be exposed was about 95°F (35°C). Reputedly, the membranes hydrolyze rapidly at higher temperature. However, operation at elevated temperature not only would result in greater flux rates, but also would reduce or eliminate the expensive preparatory operation of cooling. Hence, the vendors were invited to provide small pilot units for operation on uncooled feed at a temperature of approximately 50°C.

The first unit operated was a single tubular module (36 $ft^2$) fed by a separate pump. It was operated for 694 hours; the flux rate did not decay greatly and the product water quality remained good. This success led to the installation of a second unit, again tubular, with 72 $ft^2$ of membrane surface.

This unit operated for a total 2048 hours on feed that averaged about 122°F (50°C). There were many mechanical problems, such as excessive wear on the small pump and distortion of plastic components. The flux rate declined gradually until 40 percent was lost in the first 1000 hours of operation. During the second 1000 hours, the decline was only 10 percent more.

It was found that the flux rate varied more widely than with the cooled unit. Physically, a very dense fouling was observed that accumulated and sloughed off in a different manner from the fouling in the cooled unit. The product water quality did not deteriorate in any property and the rejection did not change. For example, the percent rejection of $BOD_5$ was 99.67 percent in the 53rd hour of operation, and 99.66 percent after 1740 hours more exposure. Operations were terminated because of thermal deformation of the module, but no membrane deterioration was experienced.

The second vendor provided a small unit with spiral-wound modules. This was operated at approximately 122°F (50°C) for a total of 1267 hours. The flux rate declined rapidly in the first 150 hours of operation, until about 60 percent of the original rate was lost. The productivity then remained essentially constant until operation was terminated. Again, mechanical problems caused the cessation. No membrane deterioration was experienced.



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The product water quality on this unit remained excellent with no change in the percent rejection. After the first 800 hours of operation, the modules were visually inspected and found to be very heavily fouled; and yet the pressure drop had not increased nor the membrane productivity decreased proportionately when compared to the results of operating the cool spiral-wound unit.

Both types of hot units were operated with the same velocities, depressurization cycles, etc., that were in use with the main units processing cooled waste. The excellent condition of the membranes after high temperature exposure implies that either the commonly recognized temperature limitation is invalid or that a property in the feed inhibited the rate of hydrolyzation. Regardless of the reason, any further field investigation of reverse osmosis should include some exposure at higher temperature if this is a normal process condition.

# SECTION XI

## EQUIPMENT EVALUATION

One of the goals of the pilot phase of the project was to evaluate proprietary reverse osmosis equipment. The purpose of the evaluation was to assess the capabilities of the reverse osmosis process as applied at Green Bay Packaging as well as to judge whether or not individual vendors could meet the equipment qualification standards established by the project. The evaluation was based primarily on the three-month "frozen design" period; but, to keep performance in the proper perspective, reference will be made to operations carried out in the pretrial period.

Comparisons among the several vendors of the membrane productivities are not made for several reasons. The anticipated production plant will be judged on each vendor's total design and total cost, regardless of membrane surface area. A flux rate was not specified to the vendors for the trial period. They were free to set conditions, such as operating pressure, to obtain the best information for the purpose of production plant design. The pilot plants were constructed for data acquisition and did not necessarily reflect an arrangement for optimum flux rate.

With one exception noted in the following section, materials of construction used in all units were found to be compatible with the cooled feed and process conditions. Arrangement of modules, fittings, and associated lines often fell short of standards for industrial service. Inconvenient connections, inferior nonproprietary equipment, inaccessible points for maintenance, inappropriate instrumentation, and poor clearance for parts removal indicate a need for improvement to cope with industrial production and maintenance demands.

The Aqua-Chem pilot plant was received in advance of the program and had been in operation since April 2, 1970. Therefore, entrance into the three-month pretrial test period on September 1, 1970, was merely a continuation of testing already in progress.

As of September 1 the modules most recently installed in the pilot plant had been exposed to 335 hours of operation processing white water. By the time this total reached 450 hours on September 6, however, enough failures had been experienced to warrant refitting the unit.

New modules were installed in the plant on September 28. Aqua-Chem warned that these modules were of questionable quality, but they were providing them so that investigations could continue. Another refitting was anticipated within 30 days. The first module failure occurred after 277 hours of operation and was attributed to a defective end seal. Module failures became increasingly regular until the run was terminated on October 28 after 670 hours of operation. At this time, 13 of the 24 modules were discharging permeate of inferior quality. Onsight inspection of the "bad" modules showed both seal and tube failures. Aqua-Chem stated that the tube failures might be attributed to variations in the tube paper used in manufacture. The pilot plant remained inoperative for the remainder of the pretrial period.

The unit was refitted with new modules on December 1, 1970, the first day of the "frozen design" period. The new modules contained tubes which were approximately 1/4" longer than those tested previously. Apparently the shorter tubes had caused the sealing problems that had been encountered. These new tubes also incorporated a new ferrule design which had been tested on several replacement tubes in the pretrial period and found to perform satisfactorily.

Operation of the unit began on December 3. After 160 hours of operation and immediately after a pause cycle, the unit began to intermittently discharge discolored permeate from all modules. Investigation revealed that the heads at the end of each module had been improperly torqued. After they were tightened, no discoloration was visible. The unit ran from this point to February 28, the end of the test period, with no more difficulty. A total of 1927 hours were logged during the "frozen" period with no module failures.

Testing continued after February 28, and the first module failure was encountered after 2044 hours of operation. Inspection of the module revealed that one of its tubes contained a manufacturing defect. The tube was replaced, but leaking continued. The plant was finally shut down after 12 of the modules had been run 3936 hours and 12 had been run 3533 hours. No new leaks were encountered before the final shutdown. Inspection of the modules revealed only a moderate amount of fouling present in the tubes and turnarounds. Inspection of the one module which did fail revealed that leaking had been caused by an irregularity in the support tube. Apparently the support tube had been damaged when the bad tube was replaced.

Operation of the American Standard pilot plant began on November 6, 1970. After 59 hours of operation, one of the 84 total modules developed a high pressure leak. The bonding which held the membrane support tube in the module head yielded, allowing the tube to back out of the head. A second failure of this type was experienced after 78 hours. American Standard stated that the bonding problem was suspected at time of shipment, and more failures were to be expected. Within a short period of time, three more bonding failures occurred. At 148 hours a sixth module failure took place, this one a low pressure leak caused by a loose head nut. The nut was tightened, and the module performed satisfactorily. As of November 30 the unit had experienced seven major module failures in a total of 450 hours of operation. Although no visual inspection of modules was made, the large flux degeneration experienced and the distinct $H_2S$ odor present in the modules indicated that the unit was heavily fouled.

The unit was restarted for "frozen design" running on December 2. Another bonding failure occurred at 219 hours into this run (669 total hours), the seventh failure of this type since the unit was originally started. The unit was shut down on March 3. It had run a total of 1447 hours during the "frozen design" period and had experienced three major module failures at the tube to module head bond during the frozen design period. No visual inspection was performed.

The Gulf Environmental Systems pilot plant was placed on line August 26. Immediately the spiral-wound unit began to experience fouling problems. After one day of operation, fouling had become so extensive that the unit was shut down. Inspection of the modules showed that the suspended materials in the white water had become entrapped in the module's process stream spacer causing excessive pressure drop across the modules and blinding the membrane surface. The unit remained down while Gulf investigated means to alleviate the problem. After pursuing several alternatives, Gulf decided to employ a new spacer design in their test modules.

Modules incorporating this new design were installed in the pilot plant on October 6, and operations were resumed. The unit was shut down three days later and the modules inspected. Fouling was significantly less than that found in the first set of modules. Two of the five modules were replaced with new modules, and the two removed were shipped to San Diego for further inspection.

The unit was restarted and ran without incident until November 2, when it was shut down for inspection. During this time, it had become necessary to flush the unit with tap water periodically and to clean with an enzyme solution occasionally to deter excessive fouling. When the modules were inspected, they were found to contain a great deal of internal fouling. The annular space between modules and support pipe was filled with slime. Also, the adhesive backing tape, used to maintain module configuration, had deteriorated somewhat. In a test just prior to shut-down, the unit had been exposed to a cationic polymer which seemed to do more harm than good and probably contributed greatly to the fouled state of the modules. The modules were rinsed manually and placed back in the unit. Operation was resumed and continued until November 5 when the unit was shut down for refitting. These modules were exposed to a total of 532 hours on white water.

New modules of the same configuration were placed in the unit, and it was restarted on November 6. Immediate discoloration of the permeate on restart indicated that either a defective module had been installed or an o-ring seal between modules had been broken on reassembly. The situation remedied itself, so operation was not interrupted. The problem was attributed to a seal which had slipped out of place and then reseated itself. The unit operated without difficulty for 391 hours and was shut down on November 25. Throughout the last part of this run, a distinct $H_2S$ odor had been present in the permeate indicating sliming in the unit. Inspection of the modules proved this to be the case.

A completely new pilot plant was received from Gulf for the "frozen design" period. This unit was equipped with modules which incorporated the new spacer design concept, but with a dimensional change. Several different types of backing tapes were also used in an effort to find one which would not loosen after extensive running. Three of the 18 modules were externally wrapped so as to provide flow around the modules to eliminate accumulations in the dead annular space. An automatic backflush was included as standard operating procedure.

The unit was started up on November 30. After 78 hours the modules were inspected, and both interior and annular fouling were found to be minimal. As operations continued, it became necessary to clean the unit with an enzyme solution approximately every 150 hours. After 1042 hours of trouble-free operating, the unit was shut down for another inspection; fouling was present but was not

extensive. Three modules were replaced at this time, and the modules removed were sent to San Diego for testing. When the unit reached 1132 hours of operation, it began to intermittently discharge discolored permeate. After 1259 total hours had elapsed, it was shut down so that the problem could be investigated. The investigation revealed a broken o-ring seal between two modules. Gulf stated that this problem is often encountered when modules are changed, but it may take time to expose itself. The o-ring was replaced, and operation was resumed. Sixteen hours later the same tube began to discharge discolored permeate; the leak was traced to another bad o-ring. The unit was restarted and run to a total of 1425 hours before it was shut down due to excessive fouling. Inspection of the modules showed great amounts of fouling at the module faces and in the tube turnarounds.

The unit was completely refitted with new modules. Three of the new modules were installed such that the velocity through them would be double that of the others. After several false starts (two o-rings failed and one defective module was replaced), the unit was run for 585 hours without incident and was shut down on March 17. Later inspection of the modules by the vendor showed that the high velocity modules exhibited greatly reduced fouling characteristics.

The Havens pilot unit was placed in operation for the pretrial period on September 11. It ran without failure until November 12, logging 1071 hours. Inlet pressure was maintained at 600 psi. Fouling did not appear to be a problem.

Testing in the "frozen design" period was initiated on December 4. Inlet pressure was 800 psi. The first module problem was encountered after 1133 total hours of operation on these tubes. The low volume leak was attributed to a bad tube adapter seal. Another seal leak occurred at 1333 hours, and a third such failure took place at 1650 hours. After 2014 total hours, a fourth module failed; the failure was a high volume leak but was not a tube rupture. This module was replaced with a module which had failed after 7 hours of operation. Prior to shutdown on February 10, two more modules experienced major seal leaks and others appeared to be leaking. These modules had been in operation 2100 total hours at shutdown. Havens attributed the problem to swelling of the tube adapters and decided to rebuild all the modules with adapters of the same design but of a new material. As agreed prior to the start of the tests, three months running time would be required to qualify the material. The old

heads and tubes were to be reused as possible. As the rebuild progressed, it was found that many of the heads were also swollen, so all of them were replaced with new ones. The membranes were in excellent condition.

Operation was resumed on February 27. One hundred hours after restarting, one of the modules developed a high pressure leak. Twenty-six hours later, another such failure occurred. Several more failures were encountered before the unit was shut down. It had logged 565 hours after rebuild and 2664 total hours of operation had been completed on these tubes. Inspection of the later failures by Havens showed that the adapter swelling prior to the rebuild had apparently caused a dimensional problem.

New modules and a new, smaller pilot plant were received so that the qualification time for the new material could be reached; but numerous module failures have prevented completion of the qualification.

## SECTION XII

## EQUIPMENT DISCUSSION - MECHANICAL PERFORMANCE

The pilot phase of the project demonstrated that reverse osmosis equipment is capable of processing waste water from NSSC pulping with reasonable efficiency. Membrane integrity proved to be acceptable; none of the failures experienced during the test period were attributed to membrane degradation. Analyses of membranes which had been processing white water for nearly 4000 hours (the longest membrane exposure time experienced during the project) showed that although some permanent flux deterioration had occurred, the rejection characteristics were virtually unchanged from those displayed initially. The majority of proprietary equipment problems occurred because of failures in the sealing mechanisms between membrane support structures and module heads. Most of these failures could have been eliminated had greater care been taken in module assembly, both at initial construction and during field maintenance. The results of the project indicate that continuous operation can be expected from reverse osmosis equipment if properly assembled and maintained.

During earlier pilot plant investigations, a great variation in membrane performance was experienced from module to module. Vendor production control of membrane performance was found to be greatly improved during this program. Individual modules were reasonably uniform in their membrane characteristics.

Based on the very low failure rate experienced during the "frozen design" period, all Aqua-Chem proprietary equipment has been found acceptable under the standards established by the project. The equipment was tested for 1927 hours during this period, with the only difficulty experienced being a slight seal leakage caused by improper torqueing on module heads. That problem was easily resolved.

Maintenance of proprietary equipment and identification of module failures is not difficult with this design. Individual permeate discharges on each module allow one to pinpoint failures easily, and tubes may be replaced without removing the entire module from the system. However, it is difficult to isolate a bad tube within a module; and individual modules or clusters of modules cannot be isolated from the total system. During these pilot tests, it was necessary to shut down all 24 modules in order to inspect one particular module. The module stacking

arrangement also makes it difficult to remove a module from the system if that module happens to be located at the bottom of the stack.

All American Standard proprietary equipment, with the exception of the tube to module head bonding seal, has been found mechanically acceptable. It is felt that because of the eight seal failures encountered in 1897 total hours of running time, further testing would be mandatory to establish reliability.

Identification and isolation of module failures are accomplished easily with this design. Valves were provided so that banks of six modules could be taken off line while the unit remained operative. Accessibility to modules located in the middle of the cluster was somewhat difficult, and enough room must be left above the unit so that the vertically mounted modules may be removed.

All Gulf equipment met the qualification standards of the project. However, some type of periodic flushing is necessary to keep the modules free of excessive fouling. It also appeared that enzyme cleaning was necessary at 150 hour intervals in order to maintain reasonable flux rates. The only maintenance difficulty seen was the amount of care that was necessary to protect the o-ring seals. Module replacement can be performed rather easily, and identification of defective modules presents no problem. It appeared that the module binding tape was undependable after extended running time. Further demonstration of improved binding tape performance would be desirable.

All Havens equipment, with the exception of the end seal adapters, has proven acceptable. The adapter change did not involve the design. However, it is considered desirable to test the reliability of the new material, and such tests are underway. Identification of module failures is a problem, but isolation and removal of defective modules can be performed relatively easily. In several instances, difficulty was encountered in forming the 4-module clusters which comprised the unit. Improperly sized "peg holes" and variations in module length made it difficult to obtain a proper seal between modules.

# SECTION XIII

## ACKNOWLEDGMENTS

This project is being performed under the direction of Messrs. Ralph H. Scott, G. R. Webster, and W. J. Lacy of the Environmental Protection Agency. Project Director for Green Bay Packaging is Mr. W. R. Nelson; Project Manager is Mr. G. O. Walraven; and Project Engineer is Mr. D. C. Morris. Other Green Bay Packaging personnel participating extensively in the project are Messrs. S. L. Brown and M. J. Pollock, Project Engineers; Mr. T. J. Fenske, Laboratory Technician; and Miss K. R. Jackson, Secretary.

The close cooperation and assistance of the vendors is acknowledged. Key personnel were Mr. A. C. P. Ammerlaan, Abcor; Mr. D. B. Guy, Aqua-Chem; Mr. J. H. Sleigh, Gulf; and Mr. K. E. Anderson, Calgon-Havens.

The long-standing support of the staff of the Institute of Paper Chemistry is gratefully acknowledged.

SECTION XIV

APPENDICES


| | | Page No. |
|---|---|---|
| A. | Analytical and Test Procedures Used in Pilot Phase . . . . . | 86 |
| B. | Visitors Observing Pilot Units in Operation Since Initiation of Project 12040 PUB . . . . | 88 |


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## APPENDIX A

## ANALYTICAL AND TEST PROCEDURES USED IN PILOT PHASE

The analytical samples were collected when the operating conditions of the units were stable. This required that the samples be taken at the middle of each pause-operate-pause cycle, since the conditions close to the depressurization (pause) period were not representative of the majority of the operating period. Operating data, e.g. pressures, were recorded at the time of taking samples. When samples were collected at inconvenient hours, they were refrigerated for storage and then returned to room temperature before analysis.

Frequent measurements were made of the total solids in the feed and concentrate. The sample is weighed in an oven-dried tared beaker, dried overnight at 105°C, cooled in a desiccator, and reweighed.

Soluble solids and suspended solids were determined by a method developed at Green Bay Packaging. A sample is filtered through a glass fiber pad (Reeve Angel 934 AH, 11 cm), and the filtrate is collected. The pad is oven-dried, cooled in a desiccator, and reweighed for suspended solids. The filtrate is weighed in an oven-dried tared beaker, dried overnight at 105°C, cooled in a desiccator, and reweighed for soluble solids. Samples of product water from the reverse osmosis units required no filtering.

Sodium content was determined with a Model 303 Perkin-Elmer atomic absorption spectrophotometer. The sample is prepared to the proper working range using distilled water for dilution. The spectrophotometer is operated according to Perkin-Elmer's Analytical Methods Manual.

Analysis for five-day biochemical oxygen demand ($BOD_5$) was performed according to the procedures, chemical requirements, and apparatus described in Standard Methods for the Examination of Water and Waste Water (APHA-AWWA-WPCF) using the Azide Modification of Iodometric (Winkler) Method. The sample is prepared per this reference with the exception of measuring the initial dissolved oxygen. In lieu of this measurement, a dilution water blank containing all the nutrients, seed, and dissolved oxygen is incubated with each set of samples to eliminate any dilution water variables. Volumetric flasks and pipettes are utilized for measurement and dilution. A sample two

cubic centimeters or larger is pipetted directly into the BOD bottle.

Color was performed using two methods by the Institute of Paper Chemistry. The first measurement was a visual observation of the color utilizing a Hellige optical comparator. This technique is not precise and was done for reference purposes only. The second measurement was of the optical density, utilizing a Beckman DU spectrophotometer operated at the nominal wavelength range for lignins (281 millimicrons).

APPENDIX B

VISITORS OBSERVING PILOT UNITS IN OPERATION

SINCE INITIATION OF PROJECT 12040 FUB

| Number | Organization or Affiliation |
|---|---|
| | U. S. Industrial Companies |
| 4 | American Can Company |
| 1 | Anheuser-Busch, Inc. |
| 3 | Charmin Paper Products Division, Proctor & Gamble |
| 2 | Combined Paper Mills, Inc. |
| 1 | Corning Glass |
| 1 | Dart Industries, Inc. |
| 2 | C. H. Dexter Paper Company |
| 6 | Dorr-Oliver, Inc. |
| 2 | Eastman Chemical |
| 5 | Esso Research & Engineering Company |
| 1 | The Foxboro Company |
| 1 | Groveton Papers Company |
| 2 | Industrial Nucleonics |
| 3 | Kraftco Corporation |
| 1 | Menasha Corporation |
| 1 | Nalco Chemical Company |
| 5 | Northwest Paper Company |
| 2 | Paterson Parchment Paper Company |
| 2 | Petrolite Corporation |
| 1 | Private Consultant |
| 2 | D. E. Riley Corporation |
| 2 | St. Regis Paper Company |
| 4 | Scott Paper Company |
| 1 | Sterling Pulp & Paper Company |
| 1 | Union Carbide |
| 3 | Waldorf-Hoerner |
| | Foreign Concerns |
| 3 | Abitibi Paper Company Ltd. (Canada) |
| 1 | E. L. Bateman, Ltd. (South Africa) |
| 15 | Canadian Pulp and Paper Association, Technical Subcommittee |
| 2 | Central Association of Finnish Wood Using Industries |
| 5 | Daishowa Paper Company (Japan) |
| 1 | Finnish Pulp & Paper Research Institute |

| | | |
|---|---|---|
| 2 | | AB Iggesunds Bruk (Sweden) |
| 2 | | C. Itoh & Company (America), Inc. (Japan) |
| 2 | | Japan Organo Company, Ltd. |
| 2 | | Kurita Water Industrial Company (Japan) |
| 1 | | MacMillan Bloedel (Canada) |
| 1 | | Settsu Paper Board Manufacturing Co. (Japan) |
| 1 | | South African Pulp & Paper Industries, Ltd. |
| 1 | | Sumitomo Paper Company (Japan) |
| 1 | | Swedish Forest Products Research Laboratory |
| 1 | | Twente University of Technology (Holland) |
| 1 | | Union Corporation (South Africa) |
| 1 | | Valmet Oy (Finland) |
| | | Government |
| 5 | | Green Bay Metropolitan Sewerage District |
| 1 | | Local Elected Official |
| 2 | | State Elected Officials |
| 1 | | Federal Elected Official |
| 2 | | Wisconsin Department of Justice |
| 3 | | Wisconsin Department of Natural Resources |
| | | Education |
| 13 | | Institute of Paper Chemistry |
| 1 | | Staff, Wisconsin State University-Stevens Point |
| 10 | (Approx.) | Staff, University of Wisconsin-Green Bay |
| 15 | (Approx.) | Miscellaneous Students, University of Wisconsin-Green Bay |
| 15 | | Advanced Chemistry Students, University of Wisconsin-Green Bay |
| 15 | (Approx.) | Junior & Senior High School Students |
| | | Environmental Groups |
| 4 | | Citizens' Natural Resource Association |
| 1 | | National Council On Stream & Air Improvement |
| 15 | (Approx.) | Northeast Wisconsin Chapter, Trout Unlimited |
| | | Miscellaneous |
| 14 | (Approx.) | American Institute of Plant Engineers |

1 American Paper Institute
5 News Media (Press & TV)
18 Wisconsin Association of Food &
Sanitation Officials

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2 Subject Field & Group:

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Mill Division

6 Title
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10 Author(s)
Morris, David C.
Nelson, William R.
Walraven, Gerald O.

16 Project Designation
EPA, OR&M Program No. 12040 FUB

21 Note

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Waste Control

25 Identifiers (Starred First)
*Waste Recycle, Organic Removal, Color Removal, Membranes
Tertiary Treatment

27 Abstract
A program is in process involving the closure of a pulp and paperboard mill and includes the recycle and re-use of weak waste waters. These waste waters, containing dissolved organics, occur as a consequence of normal production methods in such a mill. A method of recycling weak waste waters has been developed and incorporated that results in the reduction and partial concentration of the waste stream. Reverse osmosis is being investigated for use as a unit operation in which clarified water is separated from the remaining wastes for process re-use, and the organics are concentrated for processing by more conventional techniques.

To ensure that the production reverse osmosis facility would reflect the latest technology, the project required a pilot phase in which reverse osmosis vendors would operate proprietary equipment simultaneously and continuously on the same feed. This preliminary phase allowed the development of operating techniques applicable to this particular feed. Criteria were determined for the design of a full-scale production facility. The proprietary equipment designs of the participating vendors were assessed. (Morris - Green Bay Packaging)

Abstractor: David C. Morris | Institution: Green Bay Packaging Inc.

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